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Nanosized Au particles as an efficient cocatalyst for photocatalytic overall water splitting

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The effect of the photodeposition of gold particles onto several photocatalysts on the photocatalytic activities was studied. The photocatalytic activities of $K_4Nb_6O_{17}$, $Sr_2Nb_2O_7$, $KTaO_3$ $NaTaO_3$, and $NaTaO_3$ doped with La for water splitting were improved when gold particles were deposited. The latter were nanoparticles, consistent with their surface plasmon absorption. The nanosized gold particle functioned as an efficient cocatalyst for photocatalytic water splitting by assisting H_2 evolution.

KEY WORDS: nanosized Au catalyst; photocatalysis; water splitting.

1. Introduction

Development of an energy system based on H_2, which is an ultimately clean form of energy, has been urged. Photocatalytic water splitting into H_2 and O_2 has drawn attention as one of the attractive H_2 production technologies. Many highly active metal oxide photocatalysts have been reported for water splitting under UV irradiation [1–3]. Titanate and niobate photocatalysts for water splitting usually require cocatalysts, because they lack active sites for H_2 evolution on their surfaces [1]. Although many unmodified tantalate photocatalysts are active for overall water splitting, their activities are drastically improved by loading with NiO cocatalysts [4]. Thus, the cocatalyst is indispensable for photocatalysts for highly efficient water splitting. Noble metals such as Pt [5–7] and Rh [8, 9], and oxides such as NiO [10], RuO_2 [3, 11], and IrO_2 [12] have been reported to be effective cocatalysts for photocatalytic water splitting. However, the well-known cocatalyst Pt is not ideal for overall water splitting, because the back-reaction between evolved H_2 and O_2 to produce water proceeds efficiently on the surface. Moreover, the number of cocatalyst materials is still limited, even though they play quite important roles in photocatalytic water splitting. Therefore, the further development of effective cocatalysts is important.

Gold had generally been regarded as an inactive metal. However, since Haruta *et al.* discovered that nanosized gold particles loaded on TiO_2 exhibit high activity for catalytic oxidation of CO [13, 14], the catalytic peformance of nanosized gold particles has been extensively studied [14]. Kamat *et al.* and Calzaferri *et al.* have found that photocurrents at TiO_2 [15] and AgCl electrodes [16] were improved by modification with nanosized gold particles. Au-loaded photocatalysts for the decomposition of nitrate ions [17], azo-dyes [18], and perchlorinated compound [19] have also been reported. There are reports of H_2 evolution on nanosized Au-loaded TiO_2 from an aqueous ethanol solution [20] and on nanosized Au-loaded $K_2La_2Ti_3O_{10}$ from water [21]. In these cases, the fine Au particles function as active sites for H_2 formation. However, there are no reports on the effectiveness of the Au cocatalyst for photocatalytic overall water splitting, i.e. to H_2 and O_2, which is much more difficult than H_2 evolution alone. Not only the creation of an active site but also the enhancement of charge separation is required of the cocatalyst, especially for water splitting. In the present study, the effects of the Au cocatalyst on photocatalytic water splitting to H_2 and O_2 are investigated.

2. Experiments

$K_4Nb_6O_{17}$, $Sr_2Nb_2O_7$, $KTaO_3$, $NaTaO_3$, and $NaTaO_3$:La photocatalyst powders were prepared according to previous reports [22–25]. Au cocatalyst particles were loaded on these photocatalysts by a photodeposition method from an aqueous solution of $HAuCl_4 \cdot 4H_2O$ (Wako Pure Chemical; 99%).

Photocatalytic reactions were carried out in a gas-tight circulation system. For the photocatalytic overall water splitting, the catalyst powder (0.3–0.5 g) was dispersed in water (350 ml) containing a certain amount of $HAuCl_4$. An inner irradiation cell made of quartz and a 400-W high-pressure Hg lamp (SEN; HL400EH-5) were

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employed. The individual reactions making up water splitting, i.e. H_2 and O_2 evolution, were also examined from aqueous solutions of methanol and silver nitrate, respectively. For the individual reactions, a top-irradiation cell with a quartz or pyrex window, and a 300-W Xe lamp (Parkin-Elmer, CERMAX LX-300BUV) were used. The amounts of evolved H_2 and O_2 were determined with gas chromatography (TCD, MS-5A, Ar carrier gas).

The gas phase back-reaction between H_2 and O_2 to produce water was also investigated. Photocatalyst powder (0.1 g) and a gas mixture of H_2 (100 torr) and O_2 (50 torr) were introduced into a gas-tight circulation system with a 350-mL dead volume. The decrease in the pressure of the gas phase was monitored by gas chromatography.

Diffuse reflectance spectra were obtained with a UV–VIS–NIR spectrometer (JASCO; Ubest-570) and were converted from reflectance to absorbance by the Kubelka–Munk method. The catalysts were also examined with a scanning electron microscope (SEM, JEOL JSM-6700F).

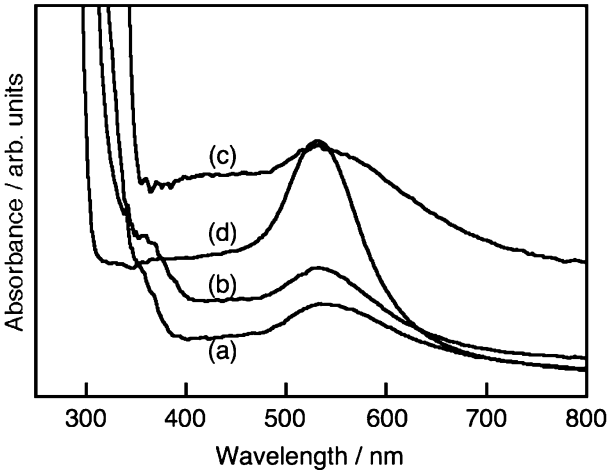

Figure 1. Diffuse reflection spectra of Au-loaded (a) $K_4Nb_6O_{17}$, (b) $Sr_2Nb_2O_7$, (c) $KTaO_3$, and (d) $NaTaO_3$:La photocatalysts.

3. Results and discussion

Table 1 shows photocatalytic activities of native and Au-loaded $K_4Nb_6O_{17}$, $Sr_2Nb_2O_7$, $KTaO_3$, $NaTaO_3$, and $NaTaO_3$:La for overall water splitting. Au-loaded $Sr_2Nb_2O_7$ and $KTaO_3$ produced H_2 and O_2, while they were not active without the Au cocatalyst. On the other hand, although $K_4Nb_6O_{17}$, $NaTaO_3$, and $NaTaO_3$:La were active even without a cocatalyst, their activities were improved by loading of Au. The loaded Au was observed as fine particles (mostly ca. 20 nm) on the photocatalyst powders (300 nm–10 μm) by SEM. In addition, the Au-loaded photocatalysts exhibited a surface plasmon absorption band around 520 nm, as shown in figure 1, also confirming that the gold was loaded as nanosized particles. Link and El-Sayed have reported the size effects on the surface plasmon absorption of spherical gold nanoparticles [26]. The sizes of Au particles loaded on photocatalysts were estimated to be 22–48 nm referring figure 1 of the Ref. [26]. This result agreed with that from SEM observation. Thus, it was found that the gold nanoparticle is able to work as an efficient cocatalyst for photocatalytic water splitting.

Figure 2 shows overall water splitting on $NaTaO_3$:La photocatalysts. Both non-loaded and Au(1 wt%)-loaded $NaTaO_3$:La photocatalysts produced H_2 and O_2 from water in a stoichiometric ratio. The photocatalytic activity of Au(1 wt%)-loaded $NaTaO_3$:La was five times higher than that of non-loaded $NaTaO_3$:La at the beginning of the reaction. However, the activity of

Table 1
Photocatalytic water splitting into H_2 and O_2 over Au-loaded oxide photocatalysts

Photocatalyst	Amount of Au loaded/wt%	Activity/μmol h^{-1}	
		H_2	O_2
$K_4Nb_6O_{17}$	None	17	5
	1	26	13
$Sr_2Nb_2O_7$	None	10	0
	2	32	14
$KTaO_3$	None	11	0
	0.5	58	25
$NaTaO_3$	None	157	60
	0.3	642	224
$NaTaO_3$:La	None	404	187
	1	1950	880

Catalyst: 0.3–0.5 g, pure water: 350 mL, 400 W High-pressure Hg lamp, inner irradiation cell made of quartz.

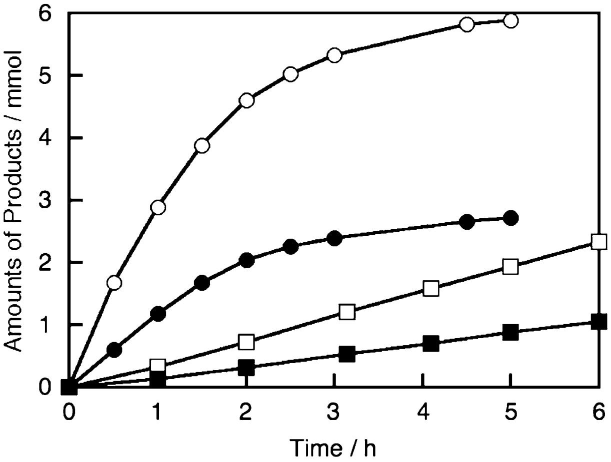

Figure 2. Photocatalytic water splitting into H_2 and O_2 over Au(1 wt%)-loaded $NaTaO_3$:La (circles) and non-loaded $NaTaO_3$:La (squares). H_2: open marks, O_2: closed marks. Catalyst: 0.5 g, pure water: 350 mL, 400 W high-pressure Hg lamp, inner irradiation cell made of quartz.

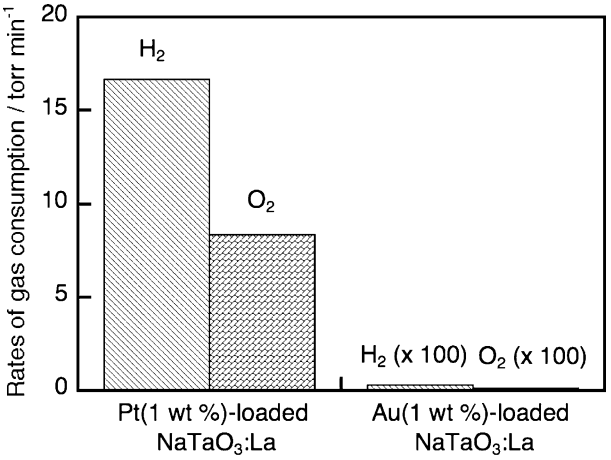

Figure 3. The rate of the reaction between gaseous H_2 and O_2 on Pt(1 wt%)-loaded NaTaO$_3$:La and Au(1 wt%)-loaded NaTaO$_3$:La in the dark. Catalyst: 0.1 g, initial pressure: H_2 100 torr, O_2 50 torr, dead volume: 350 mL.

Au(1 wt%)-loaded NaTaO$_3$:La decreased gradually. It was hypothesized that the deactivation was due to the back-reaction between evolved H_2 and O_2 and/or the photoreduction of evolved O_2 [27].

First, we studied the back-reaction between H_2 and O_2 to produce water on the Au-cocatalyst in order to examine its effect on the deactivation shown in figure 2. Figure 3 shows the rates of gas consumption on Pt(1 wt%)-loaded and Au(1 wt%)-loaded NaTaO$_3$:La powders. The pressures of H_2 and O_2 decreased very quickly on the Pt(1 wt%)-loaded NaTaO$_3$:La powders. In contrast, the reaction on Au(1 wt%)-loaded NaTaO$_3$:La was negligible. The inactivity of the Au particle cocatalyst for the back-reaction is a positive characteristic for overall water splitting, and is in contrast to the high activity of Pt. Second, we investigated the reduction of O_2 on the Au(1 wt%)-loaded NaTaO$_3$:La powder by photogenerated electrons. Oxygen gas (50 torr, which was double the pressure of evolved O_2 in overall water splitting, as shown in figure 2) was introduced into the closed system prior to the photocatalytic reaction. The activity of unmodified NaTaO$_3$:La in the presence of O_2 intentionally introduced was similar to that obtained in the absence of O_2. However, the activity of Au(1 wt%)-loaded NaTaO$_3$:La in the presence of O_2 (H_2: 157μmol h^{-1} and O_2: 73μmol h^{-1}), was smaller by one order of magnitude than that obtained in the absence of O_2 (H_2: 1950μmol h^{-1} and O_2: 880μmol h^{-1}). This result indicates that the reduction of O_2 by photogenerated electrons proceeded on the Au-cocatalyst and became predominant under a relatively high partial pressure O_2 (ca. 50 torr). It was thus revealed that the deactivation observed for Au(1 wt%)-loaded NaTaO$_3$:La in photocatalytic overall water splitting was not due to the back-reaction between evolved H_2 and O_2 but to the photoreduction of O_2 on the Au cocatalyst.

Table 2 shows photocatalytic activities of Au-loaded SrTiO$_3$ and NaTaO$_3$:La for H_2 or O_2 evolution from aqueous methanol or silver nitrate solutions, respectively. The rates of O_2 evolution at the beginning stage of photocatalytic reactions are shown. Therefore, the effect of O_2 reduction mentioned above should be negligible at the beginning stage. Au-loaded SrTiO$_3$ showed high activity for H_2 evolution from an aqueous methanol solution, as did Pt-loaded SrTiO$_3$, while non-loaded SrTiO$_3$ did not. The photocatalytic H_2 evolution on NaTaO$_3$:La was also enhanced by loading of the Au cocatalyst, while loading of the Au cocatalyst did not improve the photocatalytic activity for O_2 evolution to the extent observed after loading of Pt. It was obvious from these results that Au fine particles loaded on SrTiO$_3$ and NaTaO$_3$:La worked as active sites for H_2 formation, similar to the case for Au-loaded TiO$_2$ [20]. It was concluded that the improvement of the photocatalytic activities for overall water splitting by loading of the Au-cocatalyst was induced by introduction of active sites for H_2 formation, as observed for NiO [10] and RuO$_2$ [3, 11] cocatalysts. The enhancement of charge separation due to the injection of photogenerated electrons from the conduction band of the photocatalysts to the Au particles would also contribute to the improvement of photocatalytic performance.

4. Conclusions

The photocatalytic activities of some titanate, niobate, and tantalate photocatalysts for water splitting were improved by the loading of fine gold particles. The back-reaction between H_2 and O_2 to produce water on the Au cocatalyst was negligible in comparison with that on a Pt cocatalyst. Thus, it was found that the nanosized gold particles are effective cocatalysts on which the backward reaction of water splitting proceeds to a

Table 2

Effect of gold cocatalyst on H_2 or O_2 evolution from an aqueous solution containing a sacrificial reagent over SrTiO$_3$ and NaTaO$_3$:La photocatalysts

Photocatalyst	Cocatalyst	Activity/μmol h^{-1}	
		H_2[a]	O_2[b]
SrTiO$_3$	None	0	–
	Pt(0.1 wt%)	74	–
	Au(0.15 wt%)	75	–
NaTaO$_3$:La	None	191	44
	Pt(0.3 wt%)	345	27
	Au(0.3 wt%)	472	40

Catalyst: 0.3–0.5 g, reactant solution: 120 mL, 300 W Xe lamp, top-irradiation cell with a pyrex window for SrTiO$_3$ and a quartz window for NaTaO$_3$:La.

[a] 10 vol% of an aqueous methanol solution.

[b] 0.05 mol L^{-1} of an aqueous AgNO$_3$ solution.

negligible extent, as in the case of the NiO cocatalyst [10]. The fine gold particles play an important role in the creation of active sites for H_2 evolution and the enhancement of charge separation.

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