

# H<sub>2</sub> evolution from an aqueous methanol solution on SrTiO<sub>3</sub> photocatalysts codoped with chromium and tantalum ions under visible light irradiation

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## Abstract

SrTiO<sub>3</sub> photocatalysts doped with chromium ions showed photocatalytic activities for H<sub>2</sub> evolution from an aqueous methanol solution under visible light irradiation. However, it had a long induction period. Codoping of niobium or tantalum ions with chromium ions shortened the induction period, and increased the photocatalytic activities in respect of the H<sub>2</sub> evolution. The photocatalytic activities of chromium- and chromium/tantalum-doped SrTiO<sub>3</sub> were improved when they were pretreated at 773 K in the hydrogen reduction atmosphere. Codoping of tantalum ions suppressed the formation of Cr<sup>6+</sup> ions and oxygen defects which would work as nonradiative recombination centers between photogenerated electrons and holes, resulting in the shortening of induction periods and the improvement of photocatalytic activities.

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## 1. Introduction

Photocatalytic water splitting has attracted attention from a view point of photon energy conversion. It has been reported that some metal oxide photocatalysts are active for evolution of H<sub>2</sub> and O<sub>2</sub> from water [1–4]. Especially, the NiO/NaTaO<sub>3</sub>:La photocatalyst can decompose water into H<sub>2</sub> and O<sub>2</sub> with a high quantum efficiency, ≈50% [4]. However, these photocatalysts are not appropriate for the solar energy conversion because the highly efficient overall water splitting on the photocatalysts is limited under UV irradiation. Therefore, the development of visible-light-driven photocatalysts for water splitting is an important research target. Some metal oxides [1,2,5–7], (oxy)sulfides [1,2,8–11], and (oxy)nitrides [12–15] function as active photocatalysts for H<sub>2</sub> and O<sub>2</sub> evolution from aqueous solutions containing suitable sacrificial electron acceptors and donors under visible light irradiation. However, the highly active photocatalyst for water splitting under visible light irradiation has not been developed so far. Metal oxides are the hopeful

materials for photocatalysts aiming at water splitting owing to their stability in water.

It has been reported that WO<sub>3</sub> [1,2], RbPb<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> [1], BiVO<sub>4</sub> [1,2], Bi<sub>2</sub>WO<sub>6</sub> [2], chromium/antimony-doped TiO<sub>2</sub> [5], AgNbO<sub>3</sub> [6], and Ag<sub>3</sub>VO<sub>4</sub> [7] are visible-light-driven photocatalysts for O<sub>2</sub> evolution from water containing a sacrificial reagent. On the other hand, there are few reports of active metal oxide photocatalysts for H<sub>2</sub> evolution with visible light response, Pt/HPb<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> [1] and chromium/antimony-doped SrTiO<sub>3</sub> [5]. Therefore, the development of highly efficient metal oxide photocatalysts for H<sub>2</sub> evolution under visible light irradiation is an attractive theme. The authors have previously reported that TiO<sub>2</sub> and SrTiO<sub>3</sub> codoped with chromium and antimony ions are active for O<sub>2</sub> and H<sub>2</sub> evolution from water containing sacrificial reagents under visible light irradiation, respectively [5]. The authors have suggested in the previous paper that a concern for the charge balance is important for the design of photocatalysts doped with foreign elements.

SrTiO<sub>3</sub> is one of the candidates for the host material for the design of visible-light-driven photocatalysts possessing the H<sub>2</sub> production ability by doping of transition metal ions since the conduction band level of SrTiO<sub>3</sub> is more negative than that of rutile-TiO<sub>2</sub> [16]. On the other hand, the visible

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light response of doped SrTiO<sub>3</sub> has been reported in photoelectrochemistry [17–20].

In the present study, the photocatalytic reaction of chromium-doped SrTiO<sub>3</sub> for H<sub>2</sub> evolution from water containing methanol of a sacrificial electron donor under visible light irradiation was studied. The relationship between photocatalytic activities and the charge compensation was discussed.

## 2. Experimental

Chromium-doped SrTiO<sub>3</sub> powder was prepared by a solid state reaction. Starting materials (SrCO<sub>3</sub> (Kanto Chemical; 99.9%), TiO<sub>2</sub> (Soekawa Chemical; 99.9%), Cr<sub>2</sub>O<sub>3</sub> (Kanto Chemical; 98.5%), V<sub>2</sub>O<sub>5</sub> (Wako Pure Chemical; 99.0%), Nb<sub>2</sub>O<sub>5</sub> (Kanto Chemical; 99.95%), Ta<sub>2</sub>O<sub>5</sub> (Rare Metallic; 99.99%), and WO<sub>3</sub> (Nacali Tesque; 99.5%)) were mixed at once according to the ratio SrM<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (M: dopant element). The mixture was calcined at 1423 K for 20 h in air using a platinum crucible. The obtained powder was confirmed by X-ray diffraction using Cu K $\alpha$  radiation (Rigaku: RINT-1400). H<sub>2</sub> reduction treatment was performed on the catalyst if necessary. A platinum cocatalyst was loaded from an aqueous H<sub>2</sub>PtCl<sub>6</sub> solution by a photodeposition method.

Photocatalytic properties were evaluated by the H<sub>2</sub> evolution from an aqueous methanol solution under visible light irradiation. The photocatalytic reactions were carried out in a gas-closed circulation system. The catalyst (1 g) was dispersed in a reactant solution (310 ml) by a magnetic stirrer. An argon gas (50 Torr) was introduced into the system after deaeration. The light source was an ozone-free Xe arc lamp (Perkin-Elmer: CERMAX-LX300) attached with a cut-off filter (HOYA: Y44). The amount of evolved H<sub>2</sub> was determined using gas chromatography (Shimadzu: GC-8A, MS-5A column, TCD, Ar carrier).

Diffuse reflection spectra were obtained using a UV-Vis-NIR spectrometer (Jasco: UbestV-570) and were converted from reflection to absorption by the Kubelka-Munk method. X-ray photoelectron spectra were measured using an X-ray photoelectron spectrometer (Shimadzu: ECSA-3200). The catalysts were observed by a scanning electron microscope (Hitachi: S-5000).

## 3. Results

### 3.1. Photocatalytic activities of chromium- and chromium/M<sup>n+</sup>-doped SrTiO<sub>3</sub>

Table 1 and Fig. 1 show photocatalytic H<sub>2</sub> evolution from an aqueous methanol solution over chromium- and chromium/M<sup>n+</sup>-doped SrTiO<sub>3</sub> under visible light irradiation. All catalysts except for chromium/vanadium-doped SrTiO<sub>3</sub> produced H<sub>2</sub>. The chromium-doped SrTiO<sub>3</sub> photocatalyst steadily evolved H<sub>2</sub> after a long induction period

Table 1

Photocatalytic H<sub>2</sub> evolution from an aqueous methanol solution over chromium-doped SrTiO<sub>3</sub> under visible light irradiation<sup>a</sup>

Dopant (amount)	Rate of H <sub>2</sub> evolution ( $\mu\text{mol h}^{-1}$ )
Cr (1 mol%)	2.5
Cr (1 mol%), V (1 mol%)	0.0
Cr (1 mol%), Nb (1 mol%)	8.2
Cr (1 mol%), Ta (1 mol%)	15
Cr (2 mol%), W (1 mol%)	5.6

<sup>a</sup> Catalyst: 1 g, Pt (1 wt.%) loaded; reactant solution: 6.5 vol.% methanol, 310 ml; light source: 300 W Xe lamp attached with a cut-off filter ( $\lambda > 440$  nm).

(ca. 50 h). The photocatalytic activity of chromium-doped SrTiO<sub>3</sub> was increased when high-valent ions, such as niobium, tantalum, and tungsten ions, were codoped with chromium ions. Moreover, their induction periods became 2–3 h. However, the photocatalytic activity was disappeared when vanadium ions were codoped. Tantalum was the most effective codopant. Therefore, further investigation was carried out for the most active chromium/tantalum-codoped SrTiO<sub>3</sub> photocatalysts.

### 3.2. Effect of codoping of tantalum ions into chromium-doped SrTiO<sub>3</sub> on photocatalytic properties

Fig. 2 shows dependence of photocatalytic activities of SrTiO<sub>3</sub> doped with chromium and chromium/tantalum upon the amounts of dopants. The equimolar amounts of tantalum to chromium were codoped in the case of chromium/tantalum-doped SrTiO<sub>3</sub>. The photocatalytic activities of chromium- and chromium/tantalum-doped SrTiO<sub>3</sub> were increased as the amounts of chromium doped were larger. Although their activities reached maxima at 6% for chromium-doped SrTiO<sub>3</sub> and at 3% for chromium/tantalum-doped SrTiO<sub>3</sub>, respectively, further amounts of doping decreased the activities. Chromium/tantalum-doped SrTiO<sub>3</sub> showed higher activity than chromium-doped

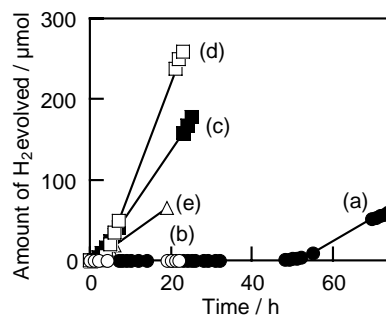


Fig. 1. Photocatalytic H<sub>2</sub> evolution from an aqueous methanol solution over chromium-doped SrTiO<sub>3</sub> under visible light irradiation. Doped with (a) Cr (1 mol%), (b) Cr (1 mol%)/V (1 mol%), (c) Cr (1 mol%)/Nb (1 mol%), (d) Cr (1 mol%)/Ta (1 mol%), and (e) Cr (1 mol%)/W (1 mol%). Catalyst: 1 g, Pt (1 wt.%) loaded; reactant solution: 6.5 vol.% methanol, 310 ml; light source: 300 W Xe lamp attached with a cut-off filter ( $\lambda > 440$  nm).

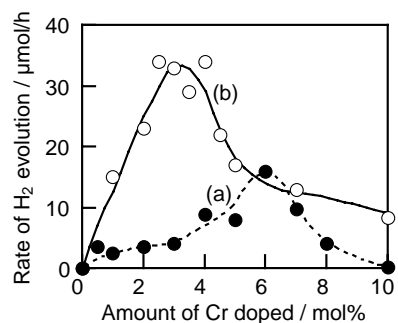


Fig. 2. Dependence of photocatalytic activities of chromium-doped SrTiO<sub>3</sub> upon the amounts of chromium. Closed circles: doped with Cr, open circles: doped with Cr/Ta. Catalyst: 1 g, Pt (1 wt.%) -loaded; reactant solution: 6.5 vol.% methanol, 310 ml; light source: 300 W Xe lamp attached with a cut-off filter ( $\lambda > 440$  nm).

SrTiO<sub>3</sub>. Especially, when 10 mol% of chromium was doped, chromium/tantalum-doped SrTiO<sub>3</sub> still showed the activity whereas chromium-doped SrTiO<sub>3</sub> was no longer active. The lengths of induction periods as shown in Fig. 1 did not depend on the amounts of chromium doped. The induction periods of chromium/tantalum-doped SrTiO<sub>3</sub> were 4–18 h, which were shorter than those of chromium-doped SrTiO<sub>3</sub> (18–50 h).

Effects of H<sub>2</sub> reduction treatment on photocatalytic properties of chromium- and chromium/tantalum-doped SrTiO<sub>3</sub> photocatalysts were examined. The colors of both catalysts were changed from blackish red to bright yellow by the H<sub>2</sub> reduction.

Diffuse reflection spectra of the photocatalysts are shown in Fig. 3. Chromium- and chromium/tantalum-doped SrTiO<sub>3</sub> as prepared possessed absorption bands at 520 and 700 nm in the visible region in addition to the intrinsic band gap absorption whereas H<sub>2</sub> reduction-performed photocatalysts had simple absorption bands with onsets around 530 nm and weak absorption bands at 570–700 nm attributed to d–d transition of Cr<sup>3+</sup> ions. The absorption spectra of reduced chromium-doped SrTiO<sub>3</sub> well agreed with action spectra of photocurrents of SrTiO<sub>3</sub> doped with Cr<sup>3+</sup> ions or LaCrO<sub>3</sub> [17–19]. The change in the absorption spectra implied that

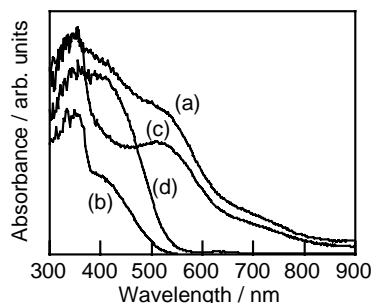


Fig. 3. Diffuse reflection spectra of chromium-doped SrTiO<sub>3</sub> with and without H<sub>2</sub> reduction treatment. (a) Cr (4 mol%) -doped, (b) reduced Cr (4 mol%) -doped, (c) Cr (4 mol%)/Ta (4 mol%) -doped, and (d) reduced Cr (4 mol%)/Ta (4 mol%) -doped.

Table 2  
Effect of H<sub>2</sub> reduction treatment upon photocatalytic activities of chromium-doped SrTiO<sub>3</sub><sup>a</sup>

Dopant (amount)	Temperature of H <sub>2</sub> reduction (K)	Induction period (h)	Rate of H <sub>2</sub> evolution (μmol h <sup>-1</sup> )
Cr (1 mol%)	None	50	2.5
Cr (1 mol%)	573	7	9.0
Cr (6 mol%)	None	15	16
Cr (6 mol%)	573	17	17
Cr (4 mol%), Ta (4 mol%)	None	16	34
Cr (4 mol%), Ta (4 mol%)	573	1	24
Cr (4 mol%), Ta (4 mol%)	773	1	70
Cr (10 mol%), Ta (10 mol%)	None	12	8.4
Cr (10 mol%), Ta (10 mol%)	573	3	7.8

<sup>a</sup> Catalyst: 1 g, Pt (1 wt.%) -loaded; reactant solution: 6.5 vol.% methanol, 310 ml; light source: 300 W Xe lamp attached with a cut-off filter ( $\lambda > 440$  nm).

Cr<sup>6+</sup> ions involved in the catalysts were reduced to Cr<sup>3+</sup> ions by the H<sub>2</sub> reduction. The photocatalytic activities for H<sub>2</sub> evolution from an aqueous methanol solution of the reduced chromium- and chromium/tantalum-doped SrTiO<sub>3</sub> were summarized in Table 2. In the case of SrTiO<sub>3</sub> doped with 1 mol% of chromium, the induction period was drastically shortened from 50 to 7 h by H<sub>2</sub> reduction treatment. In addition, the rate of H<sub>2</sub> evolution was also improved by four times by H<sub>2</sub> reduction treatment. However, no significant improvement in the photocatalytic properties by H<sub>2</sub> reduction treatment was observed in the case of 6 mol% of chromium doping. On the other hand, the induction periods of all catalysts were shortened by H<sub>2</sub> reduction treatment when tantalum ions were codoped with chromium ions. The activities were not improved in the case of H<sub>2</sub> reduction performed at 573 K whereas the activity was increased by two times in the case of H<sub>2</sub> reduction performed at 773 K. The photocatalytic H<sub>2</sub> evolution from an aqueous methanol solution over the most active photocatalyst, chromium(4%)/tantalum(4%)-doped SrTiO<sub>3</sub> reduced by H<sub>2</sub> at 773 K, under visible light irradiation ( $\lambda > 440$  nm) is shown in Fig. 4. After 1 h of an induction period, H<sub>2</sub> evo-

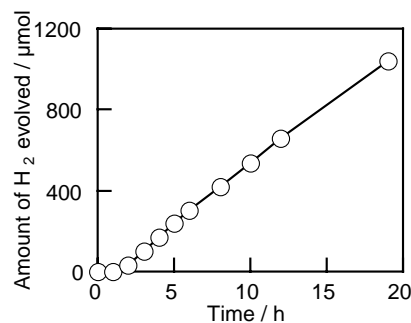


Fig. 4. Photocatalytic H<sub>2</sub> evolution from an aqueous methanol solution over Cr (4 mol%)/Ta (4 mol%)-doped SrTiO<sub>3</sub> reduced with H<sub>2</sub> at 773 K under visible light irradiation. Catalyst: 1 g, Pt (1 wt.%) -loaded; reactant solution: 6.5 vol.% methanol, 310 ml; light source: 300 W Xe lamp attached with a cut-off filter ( $\lambda > 440$  nm).

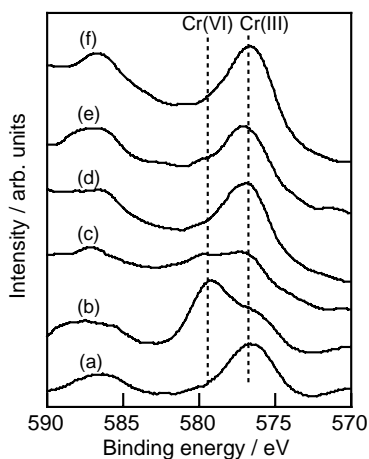


Fig. 5. X-ray photoelectron spectra of Cr 2p of (a)  $\text{Cr}_2\text{O}_3$ , (b)  $\text{CrO}_3$ , (c) Cr (4 mol%)-doped, (d) reduced Cr (4 mol%)-doped, (e) Cr (4 mol%)/Ta (4 mol%)-doped, and (f) reduced Cr (4 mol%)/Ta (4 mol%)-doped  $\text{SrTiO}_3$ .

lution steadily proceeded. The amount of  $\text{H}_2$  evolved for 19 h of irradiation was reached  $1040 \mu\text{mol}$ . It is much larger than the amounts of chromium and tantalum ( $193 \mu\text{mol}$ ) involved in 1 g of the catalyst. It indicates that the  $\text{H}_2$  evolution proceeded photocatalytically by the excitation of the visible light absorption band due to transition from the electron donor level formed with doped chromium ions to the conduction band of the  $\text{SrTiO}_3$  host.

X-ray photoelectron spectroscopy measurements were carried out in order to see the oxidation states of doped chromium as shown in Fig. 5. The peak intensity of  $\text{Cr}^{6+}$  was almost the same as that of  $\text{Cr}^{3+}$  in the chromium-doped  $\text{SrTiO}_3$  as prepared. In contrast, in the cases of chromium/tantalum-doped  $\text{SrTiO}_3$  as prepared and reduced chromium-doped  $\text{SrTiO}_3$ , the majority of chromium ions were  $\text{Cr}^{3+}$ , but small amounts of  $\text{Cr}^{6+}$  seemed to exist. On the other hand, only  $\text{Cr}^{3+}$  was detected in the reduced chromium/tantalum-doped  $\text{SrTiO}_3$ .

## 4. Discussion

### 4.1. Photocatalytic activities of chromium- and chromium/ $M^{n+}$ -doped $\text{SrTiO}_3$

If  $\text{Ti}^{4+}$  ions in the  $\text{SrTiO}_3$  lattice are replaced by  $\text{Cr}^{3+}$  ions,  $\text{Cr}^{6+}$  ions ( $\text{SrTi}^{\text{IV}}_{1-3x}\text{Cr}^{\text{III}}_{2x}\text{Cr}^{\text{VI}}_x\text{O}_3$ ) and/or oxygen defects ( $\text{SrTi}^{\text{IV}}_{1-2x}\text{Cr}^{\text{III}}_{2x}\text{O}_{3-x}$ ) should form to maintain the charge balance.  $\text{Cr}^{6+}$  ions which possess the strong oxidizing ability are able to capture photogenerated electrons. The reduction process forming  $\text{Cr}^{3+}$  and/or  $\text{Cr}^{4+}$  from  $\text{Cr}^{6+}$  seems to induce the long induction period as shown in Fig. 1. In addition, the oxygen defects may work as recombination centers between photogenerated electrons and holes resulting in the decrease in the photocatalytic activity. The formation of the  $\text{Cr}^{6+}$  ions and oxygen defects would be suppressed when high-valent cations such as  $\text{V}^{5+}$ ,

$\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ , and  $\text{W}^{6+}$  are codoped with chromium ions to compensate the unbalanced charge as had been discussed in the previous paper [5]. Nevertheless, in the case of chromium/vanadium codoping, the photocatalytic activity was negligible. Because V 3d orbitals should form a trapping level below the conduction band consisting of Ti 3d.  $\text{V}^{5+}$  ions trap the photogenerated electrons resulting in formation of  $\text{V}^{4+}$  ions which facilitate the charge recombination. In addition, the local structure around  $\text{V}^{5+}$  ions might be distorted because of their small ionic radii. Such a local distortion would also work as charge recombination centers. Codoping of tungsten ions did not increase the rate of  $\text{H}_2$  evolution as much as codoping of niobium and tantalum ions. It is also due to the electron trap and a positive shift in the conduction band by tungsten ions. However, a significant effect on shortening of the induction period was observed. It indicates that codoping of tungsten ions certainly compensated the unbalanced charge. In contrast to them, it is considered that codoping of niobium and tantalum ions can achieve the charge compensation without the positive shift in the conduction band, resulting in the shortening of induction periods and the increase in the rate of  $\text{H}_2$  evolution.

### 4.2. Effect of codoping of tantalum ions into chromium-doped $\text{SrTiO}_3$ on photocatalytic properties

The photocatalytic activities of chromium- and chromium/tantalum-doped  $\text{SrTiO}_3$  were increased, reached maxima, and then decreased as the amounts of chromium doped became larger, as shown in Fig. 2. The number of photons absorbed would be increased with the increase in the amounts of chromium, resulting in the increase in the activities. On the other hand, doping of a large amount of chromium ions would facilitate the charge recombination. Therefore, these factors gave the optimum amounts of dopants. The formation of the charge recombination centers such as  $\text{Cr}^{6+}$  ions and oxygen defects is inevitable when  $\text{SrTiO}_3$  is doped with only chromium ions as mentioned above. In contrast, codoping of tantalum ions with chromium ions prevents from the formation of such charge recombination centers since two  $\text{Ti}^{4+}$  ions are ideally replaced by a couple of  $\text{Cr}^{3+}/\text{Ta}^{5+}$  ( $\text{SrTi}^{\text{IV}}_{1-2x}\text{Cr}^{\text{III}}_x\text{Ta}^{\text{V}}_x\text{O}_3$ ). In the cases of doping with chromium of 10 mol%, the chromium/tantalum-doped  $\text{SrTiO}_3$  was still active whereas chromium-doped  $\text{SrTiO}_3$  was no longer active. It is due to the suppression of the formation of the recombination centers caused by codoping of tantalum ions. On the other hand, changes in particle sizes and surface morphology as observed in the  $\text{NaTaO}_3:\text{La}$  was not observed for the present system [4]. It was revealed from XPS measurements that the formation of  $\text{Cr}^{6+}$  ions was suppressed by codoping of tantalum (Fig. 5). The absorption at 520 and 700 nm was strong in the catalysts containing a large amount of  $\text{Cr}^{6+}$  ions (Fig. 3). These bands were disappeared when  $\text{H}_2$  reduction pretreatment was performed. Thus, the relationship between the absorbance at 520 and 720 nm and the amount of  $\text{Cr}^{6+}$  ions was observed. It is considered that

the absorption bands are due to complicated transition related to the SrTiO<sub>3</sub> host, Cr<sup>3+</sup>, and Cr<sup>6+</sup> ions. On the other hand, the XPS of reduced chromium-doped SrTiO<sub>3</sub> was similar to that of chromium/tantalum-doped SrTiO<sub>3</sub> as prepared rather than that of the reduced chromium/tantalum-doped SrTiO<sub>3</sub>, indicating the existence of Cr<sup>6+</sup> ions. However, the both reduced catalysts showed similar DRS without the absorption bands due to Cr<sup>6+</sup> ions. The oxidation of a part of Cr<sup>3+</sup> ions at the surface to Cr<sup>6+</sup> ions by exposing to air is reasonable for reduced chromium-doped SrTiO<sub>3</sub> since the charge balance has to be kept by the formation of Cr<sup>6+</sup> ions and/or oxygen defects as described above. On the other hand, although the XPS of reduced chromium-doped SrTiO<sub>3</sub> and chromium/tantalum-doped SrTiO<sub>3</sub> as prepared were almost the same, their DRS were quite different from each other. It is due to that Cr<sup>6+</sup> ions were formed only at the surface in the former catalyst while Cr<sup>6+</sup> ions existed not only at the surface but also in the bulk in the latter.

The order of lengths of induction periods was chromium-doped SrTiO<sub>3</sub> > chromium/tantalum-doped SrTiO<sub>3</sub> ≈ reduced chromium-doped SrTiO<sub>3</sub> > reduced chromium/tantalum-doped SrTiO<sub>3</sub>. It corresponds to the order of the amounts of Cr<sup>6+</sup> involved in the catalysts. The induction period of the reduced chromium-doped SrTiO<sub>3</sub> was relatively long. It is due to the surface Cr<sup>6+</sup> ions formed by exposing to air after H<sub>2</sub> reduction as described above. Moreover, the photocatalytic activity of reduced chromium-doped SrTiO<sub>3</sub> was lower than that of reduced chromium/tantalum-doped SrTiO<sub>3</sub>. It is due to the oxygen defects formed in the reduced chromium-doped SrTiO<sub>3</sub> crystal in order to compensate the unbalanced charge as described above. In contrast, when tantalum ions are codoped with chromium ions in the equimolar ratio to chromium ions, the charge balance is able to be maintained without the formation of Cr<sup>6+</sup> ions and oxygen defects, resulting in that the shorter induction periods and higher activities have been observed for reduced chromium/tantalum-doped SrTiO<sub>3</sub> than reduced chromium-doped SrTiO<sub>3</sub>.

Thus, the charge compensation by codoping of tantalum ions with chromium ions has shown significant effects on the suppression of the formation of charge recombination centers such as Cr<sup>6+</sup> ions and oxygen defects resulting in the improvement in the photocatalytic properties under visible light irradiation. The authors have previously reported that chromium/antimony-doped TiO<sub>2</sub> and SrTiO<sub>3</sub> have shown the high photocatalytic activities under visible light irradiation [5]. In these cases, a couple of Cr<sup>3+</sup>/Sb<sup>5+</sup> keeps the charge balance in the titanate crystals. In the present study, it has been found that niobium and tantalum ions are also efficient codopants to maintain the charge balance as the low valent ions such as Cr<sup>3+</sup> are doped into titanate hosts. In addition, the effects of codoping on photocatalytic properties were shown more clearly in the present study than the previous report by the investigation into the dependence of activities upon amounts of dopants. The chromium/tantalum-doped SrTiO<sub>3</sub> photocatalyst con-

tributes to the Z-scheme system combined with a WO<sub>3</sub> photocatalyst for a water splitting reaction [21].

## 5. Conclusion

The chromium/niobium- and chromium/tantalum-doped SrTiO<sub>3</sub> showed the higher activities and shorter induction periods than chromium-doped SrTiO<sub>3</sub>. It was found from XPS measurements that the formation of Cr<sup>6+</sup> ions which would work as the charge recombination centers was suppressed by codoping of tantalum ions. The chromium/tantalum-doped SrTiO<sub>3</sub> still showed higher activity than chromium-doped SrTiO<sub>3</sub> even when H<sub>2</sub> reduction was conducted to reduce Cr<sup>6+</sup>. It is due to that the formation of oxygen defects was also suppressed by codoping of tantalum ions since the charge balance in the crystals was maintained by substitution of a couple of Cr<sup>3+</sup>/Ta<sup>5+</sup> for two Ti<sup>4+</sup> ions. Thus, it has been found that niobium and tantalum ions are efficient codopants to maintain the charge balance when titanate photocatalysts are modified by doping of the low valence ions such as Cr<sup>3+</sup>.

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## References

- [1] K. Domen, J.N. Kondo, M. Hara, T. Takata, Bull. Chem. Soc. Jpn. 73 (2000) 1307 (and references therein).
- [2] A. Kudo, Catal. Surv. Asia 7 (2003) 31 (and references therein).
- [3] J. Sato, N. Saito, H. Nishiyama, Y. Inoue, J. Phys. Chem. B 107 (2003) 7965.
- [4] H. Kato, K. Asakura, A. Kudo, J. Am. Chem. Soc. 125 (2003) 3082.
- [5] H. Kato, A. Kudo, J. Phys. Chem. B 106 (2002) 5029.
- [6] H. Kato, H. Kobayashi, A. Kudo, J. Phys. Chem. B 106 (2002) 12441.
- [7] R. Kouta, H. Kobayashi, H. Kato, A. Kudo, Phys. Chem. Chem. Phys. 5 (2003) 3061.
- [8] A. Kudo, A. Nagane, I. Tsuji, H. Kato, Chem. Lett. 31 (2002) 882.
- [9] A. Kudo, I. Tsuji, H. Kato, Chem. Commun. (2002) 1958.
- [10] A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Am. Chem. Soc. 124 (2002) 13547.
- [11] I. Tsuji, A. Kudo, J. Photochem. Photobiol. A 156 (2003) 249.
- [12] G. Hitoki, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, Chem. Commun. (2002) 1698.
- [13] G. Hitoki, A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, K. Domen, Chem. Lett. 31 (2002) 736.

- [14] A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Phys. Chem. A* 106 (2002) 6750.
- [15] K. Nukumizu, J. Nunoshige, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, K. Domen, *Chem. Lett.* 32 (2003) 196.
- [16] T. Sakata, in: N. Serpone, E. Pelizzetti, (Eds.), *Photocatalysis*, Wiley, New York, 1989, pp. 311–338.
- [17] G. Campet, M.P. Dare-Edwards, A. Hamnett, J.B. Goodenough, *Nouv. J. Chim.* 4 (1980) 501.
- [18] A. Mackor, G. Blasse, *Chem. Phys. Lett.* 77 (1981) 6.
- [19] R.U.E.T. Lam, L.G.J.D. Haart, A.W. Wiersma, G. Blasse, A.H.A. Tinnemans, A. Mackor, *Mater. Res. Bull.* 16 (1981) 1593.
- [20] M. Matsumura, M. Hiramoto, H. Tsubomura, *J. Electrochem. Soc.* 130 (1983) 326.
- [21] K. Sayama, K. Mukasa, R. Abe, Y. Abe, H. Arakawa, *Chem. Commun.* (2001) 2416.