Enhanced Visible-Light-Sensitive Two-Step Overall Water-Splitting Based on Band Structure Controls of Titanium Dioxide and Strontium Titanate

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Abstract

Visible light-induced two-step overall water-splitting was achieved by combining two types of photocatalysts, which were prepared by introducing foreign elements into rutile titanium dioxide (TiO₂) and strontium titanate (SrTiO₃) with a controlled electronic band structure. Rutile TiO₂ and SrTiO₃ were doped with chromium and tantalum (Cr,Ta-TiO₂) and with rhodium (Rh-SrTiO₃), respectively, to introduce visible-light sensitivity. Under irradiation with only visible light from a 420-nm LED lamp, the simultaneous liberation of hydrogen and oxygen with a molar ratio of ~2:1 was achieved with these two types of photocatalysts in the presence of iodate ion/iodide ion as a redox mediator.

Keywords
Titanium Dioxide, Strontium Titanate, Visible Light, Overall Water-Splitting, Two-Step Excitation

1. Introduction

Various photocatalytic materials have been evaluated for water splitting activity because the generated hydrogen (H₂) represents a clean and renewable fuel source [1] [2] [3]. Among examined materials, titanium dioxide (TiO₂) with which Fujishima and Honda first demonstrated photoinduced water-splitting [1] and strontium titanate (SrTiO₃) [4], are the most promising photocatalysts due to their abundance, nontoxicity, thermal stability and high resistance against
photo-corrosion. Despite these advantageous properties, both TiO$_2$ and SrTiO$_3$ are only sensitive to ultraviolet (UV) light and therefore requires modification for the utilization of visible light. To this end, numerous studies have examined the effects of doping foreign elements into TiO$_2$ and SrTiO$_3$ on visible-light-induced water-splitting [5] [6] [7] [8]. Although a sacrificial agent is needed, the doped TiO$_2$ and SrTiO$_3$ are able to generate either H$_2$ or oxygen (O$_2$) following irradiation with visible light (half reaction of water-splitting).

Combined systems consisting of two specific photocatalysts for H$_2$ and O$_2$ production (H$_2$-photocatalyst and O$_2$-photocatalyst, respectively) and a suitable redox mediator can function as visible-light sensitive photocatalysts for overall water-splitting (termed two-step overall water-splitting or Z-scheme overall water-splitting) [9]-[18]. The well-known combination is platinum (Pt)-deposited chromium (Cr) and tantalum (Ta)-codoped SrTiO$_3$ or ruthenium (Ru)-deposited rhodium (Rh)-doped SrTiO$_3$ as the H$_2$-photocatalyst, and Pt-deposited tungsten trioxide (WO$_3$) or bismuth vanadate (BiVO$_4$) as the O$_2$-photocatalyst [10] [11]. The Z-scheme systems require the suitable redox mediator, such as iodate (IO$_3^-$)/iodide (I$^-$) or ferric (Fe$^{3+}$/ferrous (Fe$^{2+}$) ions. Recently, solid-state Z-scheme systems that function in the absence of a redox mediator have been reported [13]-[18].

Our group have successfully synthesized a combined system consisting of only one mother material, TiO$_2$-based photocatalysts (Pt-deposited anatase Ti$_{0.96}$Cr$_{0.02}$Ta$_{0.02}$O$_2$ (Pt/Ti$_{0.96}$Cr$_{0.02}$Ta$_{0.02}$O$_2$) and Pt-deposited rutile Ti$_{0.982}$Cr$_{0.009}$Ta$_{0.009}$O$_2$ (Pt/Ti$_{0.982}$Cr$_{0.009}$Ta$_{0.009}$O$_2$) as the H$_2$- and O$_2$-photocatalyst, respectively) and SrTiO$_3$-based photocatalysts (Ru-deposited Sr(Ti$_{0.99}$Rh$_{0.01}$)O$_3$ and Ru-deposited (Sr$_{0.99}$Na$_{0.01}$)(Ti$_{0.99}$V$_{0.01}$)O$_3$, as the H$_2$- and O$_2$-photocatalyst, respectively) [19] [20]. Based on the activities of the systems, it was conceivable that visible-light-sensitive two-step overall water-splitting system could be improved by utilizing the SrTiO$_3$- and TiO$_2$-based materials as H$_2$- and O$_2$-photocatalysts, respectively. The construction of such a system may be advantageous because they have properties, such as nontoxicity, stability, and natural abundance, which are expected to facilitate their use in industrial and practical applications by contrast with utilization of WO$_3$ or BiVO$_4$.

In the present study, we combined Cr- and Ta-codoped TiO$_2$ and Rh-doped SrTiO$_3$, and achieved the H$_2$- and O$_2$-evolution rates derived from two-step overall watersplitting ~100 times larger irradiated with 420-nm visible-light.

2. Experimental Section
2.1. Preparations of TiO$_2$-Based and SrTiO$_3$-Based Photocatalysts

Cr- and Ta-codoped rutile TiO$_2$ (Ti$_{0.986}$Cr$_{0.007}$Ta$_{0.007}$O$_2$, Cr,Ta-TiO$_2$) as an O$_2$-evolution photocatalyst was prepared by a hydrothermal synthesis method using commercial Ti(SO$_4$)$_2$ (24.0% purity, 3.97 $\times$ 10$^{-2}$ mol; Kanto Kagaku), CrCl$_3$·6H$_2$O (1.40 $\times$ 10$^{-4}$ mol; Kanto Kagaku), and TaCl$_5$ (1.40 $\times$ 10$^{-4}$ mol; Kanto Kagaku) as starting materials. The starting materials for the form of Cr,Ta-TiO$_2$ were mixed and stirred in distilled water for 30 min using a magnetic stirrer. The solutions
were treated hydrothermally in an autoclave at 140°C for 12 h, and the resulting mixtures were washed with sufficient distilled water, collected by centrifugation, and dried at 80°C overnight. The dried mixtures were calcined at 900°C for 24 h, and were then thoroughly ground using a mortar and pestle. As a reference, non-doped rutile (TiO₂) was prepared under identical conditions using only Ti(SO₄)₂.

Rh-doped SrTiO₃ (Sr(Ti₀.⁹⁹Rh₀.₀₁)O₃, Rh-SrTiO₃) was synthesized using a conventional solid-state reaction. Commercial SrCO₃ (Kanto Kagaku, purity 99.9%), TiO₂ (High Purity Chemicals, purity 99.99%), and Rh₂O₃ (Kanto Kagaku, purity 99.9%) powders were used as the starting materials. Stoichiometric amounts of the starting materials for Rh-SrTiO₃ were wet-ball-milled (200 rpm) for 20 h using zirconium dioxide (ZrO₂) balls as the milling medium in polyethylene bottles. The resulting mixture was calcined at 1000°C for 10 h and then thoroughly ground to obtain Rh-SrTiO₃ powder. As a reference, non-doped SrTiO₃ was prepared under identical conditions using only SrCO₃ and TiO₂.

The deposition of either Pt or Ru co-catalyst onto the synthesized Cr,Ta-TiO₂ or Ru-SrTiO₃ photocatalysts, respectively, was performed by a photo-deposition method. Briefly, 0.5 g of either Cr,Ta-TiO₂ or Ru-SrTiO₃ powder was first dispersed in 100 mL methanol solution (20 vol%) as a hole scavenger. The amount of H₂PtCl₆·6H₂O (98.5% purity; Kanto Kagaku) as the source of Pt needed to give a weight fraction of Pt relative to Cr,Ta-TiO₂ of 1 × 10⁻³ was weighted. Ruthenium chloride (RuCl₃·nH₂O, n was assumed to be 3), which served as the source of Ru, was weighed to give a weight fraction of Ru relative to Rh-SrTiO₃ of 7 × 10⁻³. Weighed H₂PtCl₆·6H₂O or RuCl₃·nH₂O was added to each aqueous sample suspension, which was then sufficiently deaerated using liquid nitrogen (N₂). While deaerating the suspensions, a xenon (Xe) lamp (LA-251 Xe; Hayashi Tokei) equipped with an optical filter (Y-44, Hoya) was employed for light irradiation of the suspension for 4 h. The suspension was then centrifuged, washed with distilled water, and the resulting residues were dried at 80°C overnight. The residues were ground into a fine powder using an agate mortar to obtain Pt-deposited Cr,Ta-TiO₂ (Pt/Cr,Ta-TiO₂) and Ru-deposited Rh-SrTiO₃ (Ru/Rh-SrTiO₃) photocatalyst powders.

2.2. Characterizations

The crystal structures of the prepared powders were examined by X-ray diffraction (XRD) using a PW-1700 system (Panalytical). Brunauer-Emmett-Teller (BET) surface areas were determined using a nitrogen adsorption apparatus (Micromeritics, TriStar 3000; Shimadzu). The valency of the constituent elements was measured by X-ray photoelectron spectroscopy (XPS; Axis-Ultra, Shimadzu). UV-visible absorption spectra were obtained by the diffuse reflection method using a V-650 (JASCO) spectrometer. Quantitative analyses were performed by X-ray fluorescence (XRF) using a ZSXP PrimusII system (Rigaku). A scanning transmission electron microscope (STEM, Tecnai Osiris, FEI) were used to observe the morphology of the prepared photocatalysts.
2.3. Photocatalytic Water-Splitting Tests

Two types of photocatalytic water-splitting tests (half reactions of water-splitting and two-step overall water-splitting) were performed in a gas-closed-circulation system, which was filled with argon gas (50 kPa) after deaeration. The amounts of evolved H₂ and O₂ were monitored using an online gas chromatograph (GC-8A; Shimadzu). Each time we performed the water-splitting experiments, a different amount of N₂ was detected. We repeatedly deaerated this system to a final pressure of 2.5 Pa and then introduced argon gas into the system in the same way. For these reasons, we considered that the detection of N₂ originated from the intruded air from outside, and the effect of residual O₂ (and N₂) in water was possibly excluded [19] [20] [21]. Thus, if N₂ was detected, the O₂ amount was calculated using the following equation: O₂ = obs. O₂ − (obs. N₂/0.78) × 0.21.

H₂ and O₂ evolution derived from the half reaction of water-splitting was monitored in the presence of Ru/Rh-SrTiO₃ or Pt/Cr,Ta-TiO₂ (60 mg each) with the aid of iodide ion (I⁻) (sodium iodide (NaI), 99.5% purity, 0.01 mol/L; Kanto Kagaku) or iodate ion (IO₃⁻) (sodium iodate (NaIO₃), 99.5% purity, 0.01 mol/L; Kanto Kagaku), respectively, as a sacrificial agent. The examinations were conducted in 10 mL of solution, without adjusting the pH, with constant stirring using a magnetic stirrer and under irradiation with visible light generated from a light-emitting diode (LED) lamp with a wavelength of 420 nm (420 nm-LED, LEDH60-420, Hamamatsu Photonics). Two-step overall water-splitting experiments were conducted by adding the sample powders (Ru/Rh-SrTiO₃: 10 mg, Pt/Cr,Ta-TiO₂: 50 mg) to 10 mL IO₃⁻ solution as a starting redox mediator without I⁻. The suspension was constantly stirred using a magnetic stirrer and the pH was not adjusted. The 420 nm-LED light was used for light irradiation.

3. Results and Discussion

3.1. Characterization of the Prepared Photocatalysts

Elemental analysis by XRF indicated that the molar ratio of Ti:Cr:Ta in Pt/Cr,Ta-TiO₂ was 0.994:0.002:0.004. Notably, this molar ratio was not consistent with the starting ratios used in the preparation of the photocatalyst. This discrepancy was attributed to differences in the solubility of Ti, Cr and Ta in aqueous solution under hydrothermal conditions. The analysis also indicated that the molar fraction of Pt relative to Cr,Ta-TiO₂ was 1 × 10⁻⁴. The analysis indicated that the molar ratios of Sr:Ti:Rh in Rh/Rh-SrTiO₃ was 0.493:0.493:0.014 nearly equal to the starting fractions used in the preparation. The Ru amount relative to Rh-SrTiO₃ was observed to be 1 × 10⁻².

Cr,Ta-TiO₂ was confirmed to have a single phase of rutile TiO₂, in the obtained XRD spectrum (Figure 1(a)). In addition, the XRD peaks of Cr,Ta-TiO₂ were shifted to a lower 2θ angle compared to non-doped TiO₂ (Figure 1(b)). These results are reasonable when one considers that the effective ionic radii of Ti⁴⁺, Cr³⁺, and Ta⁵⁺ (six-coordination) are 0.0605, 0.0615, and 0.064 nm,
Figure 1. XRD patterns of prepared TiO$_2$ and Cr,Ta-TiO$_2$ powders (a), and SrTiO$_3$ and Rh-SrTiO$_3$ (c). (b) and (d) are enlargements of (a) and (c), respectively.

respectively [22]. Thus, in the rutile form of the TiO$_2$ photocatalyst, Cr and Ta ions were incorporated at Ti sites. The XRD pattern of the synthesized Rh-SrTiO$_3$ powder indicated the photocatalyst formed a cubic crystal structure with a perovskite crystalline phase (Figure 1(c)). In Figure 1(d), the peak of Rh-SrTiO$_3$ shifted to a lower 2θ angle compared to non-doped SrTiO$_3$. According to Konda et al. [23], two different species of Rh (Rh$^{3+}$ (0.0665 nm, the effective ionic radius) and a Rh species with a higher oxidation state than Rh$^{3+}$, such as Rh$^{4+}$ (0.0615 nm, the same)) replaced Ti sites as dopants. Thus, we considered that Rh ions were incorporated at Ti sites in SrTiO$_3$.

XPS spectra were recorded to confirm the valency of constituent ions in Cr,Ta-TiO$_2$ and Rh-SrTiO$_3$. Figures 2(a)-2(d) show the spectra for the Ti 2p, Cr 2p, Ta 4f, and O1s orbitals, respectively, of the prepared TiO$_2$, Cr,Ta-TiO$_2$, and commercially available TiO$_2$ (99% purity, Kanto Kagaku) after calibration with the C 1s peak, derived from a conductive carbon-tape that had a binding energy of 284.5 eV. The spectra of Ti 2p of the prepared TiO$_2$ and Cr,Ta-TiO$_2$ were quite similar without any shoulder or peak at lower binding energy side (Figure 2(a)). Thus, the valency of Ti was 4+ in the prepared TiO$_2$ and Cr,Ta-TiO$_2$ [24] [25]. In contrast, the commercial TiO$_2$ had the peaks at lower binding energy side, indicating that it includes Ti$^{3+}$ [24]. The Cr 2p peaks derived from Cr$^{3+}$ (Cr 2p$_{3/2}$ at 576.9 eV and Cr 2p$_{1/2}$ at 587.0 eV [24]) and Ta 4f peaks from Ta$^{5+}$ (Ta 4f$_{7/2}$ at 26 eV and Ta 4f$_{5/2}$ at 28 eV [26]) were observed only in Cr,Ta-TiO$_2$ as shown in Figure 2(b) and Figure 2(c), respectively. In Figure 2(d), the O 1s spectra are shown, however, they contain the spectra originated from the carbon tape. So, we are unable to discuss the valency of O and oxygen defects from these spectra. However, we consider that the prepared TiO$_2$ and Cr,Ta-TiO$_2$ do not have much oxygen defects because both of them contain Ti as Ti$^{4+}$ and Cr,Ta-TiO$_2$ has Cr and Ta as Cr$^{3+}$ and Ta$^{5+}$.
Figure 2. XPS spectra for (a) Ti 2p, (b) Cr 2p, (c) Ta 4f, and (d) O 1s of the prepared TiO₂, Cr,Ta-TiO₂, and commercial TiO₂.

Figures 3(a)-3(d) show the spectra for the Sr 3d, Ti 2p, Rh 3d, and O1s orbitals, respectively, of the prepared SrTiO₃, Rh-SrTiO₃, and commercially available SrTiO₃ (99% purity, Aldrich) after calibration with the C 1s peak similarly. The Sr 3d spectrum peak positions (Sr3d½ at 132 eV and Sr 3d½ at 134 eV [27]) were quite similar among the prepared SrTiO₃, Rh-SrTiO₃, and the commercial SrTiO₃. However, the spectrum shape of Rh-SrTiO₃ was different from those of both types of SrTiO₃ (Figure 3(a)). According to Ehre et al., the Sr 3d spectrum peak positions shift to higher energy region when SrTiO₃ becomes amorphous [27]. So, the Sr-O bonding in Rh-SrTiO₃ would be looser than that in SrTiO₃. As for Ti 2p, Rh-SrTiO₃ had shoulders at higher energy side (Figure 3(b)), indicating the existence of the structure similar to Ti₂O₃ [28]. So, the oxygen defects were presumably incorporated in Rh-SrTiO₃. The Rh3d peaks were observed only in Rh-SrTiO₃ as shown in Figure 3(c). In Figure 3(d), the observed O 1s spectra contain those originated from the carbon tape. So, we are unable to discuss the valency of O and oxygen defects from these spectra. However, as mentioned above, Rh-SrTiO₃ possibly contains oxygen defects.

The UV-visible absorption spectra of TiO₂, Cr,Ta-TiO₂, Pt/Cr,Ta-TiO₂, SrTiO₃, Rh-SrTiO₃, and Ru/Rh-SrTiO₃ are shown in Figure 4. In the spectrum of Cr,Ta-TiO₂, an absorption shoulder in the visible-light region and a negligible shift of the absorption edges were observed compared to that of TiO₂. These findings indicate that the band-gap of Cr,Ta-TiO₂ did not markedly differ from that of TiO₂. In contrast, absorption in the entire range of visible light was observed for Rh-SrTiO₃, with a peak occurring at ~600 nm. Konda et al. reported the existence of two different doped Rh species as mentioned above is responsible for this spectral pattern [23]. The absorption with a peak occurring at ~600 nm
Figure 3. XPS spectra for (a) Sr 3d, (b) Ti 2p, (c) Rh 3d, and (d) O 1s of the prepared SrTiO₃, Rh-SrTiO₃, and commercial SrTiO₃.

Figure 4. UV-visible absorption spectra of TiO₂, Cr,Ta-TiO₂, Pt/Cr,Ta-TiO₂, SrTiO₃, Rh-SrTiO₃ and Ru/Rh-SrTiO₃.

originated from the higher oxidation state of the Rh species, and the one with shorter wavelength region from Rh³⁺. Also, they asserted that the band-gap of Sr(Ti₀.₉₉Rh₀.₀₁)O₃ (i.e., Rh-SrTiO₃ in the present study) is narrowed by the partial overlap of Rh 4d⁶ (Rh³⁺) and O 2p orbitals to form the VB, resulting in a negative-potential shift of the VB top, which we confirmed in our previous study [19]. After depositing either Pt or Ru onto Cr,Ta-TiO₂ or Rh-SrTiO₃, respectively, the absorption over a wider wavelength region (>400 nm) clearly increased, indicating the successful deposition of Pt or Ru.

STEM imaging of Pt/Cr,Ta-TiO₂ and Ru/Rh-SrTiO₃ are shown in Figure 5(a) and Figure 5(b), respectively. The particle sizes of Cr,Ta-TiO₂ and Rh-SrTiO₃ were estimated to have sizes of ~100 nm and ~50 nm, respectively. The difference in particle sizes reflected the BET surface areas, which were observed to be 1.4 to 2.8 m²/g for Cr,Ta-TiO₂ and Rh-SrTiO₃, respectively. Both Cr,Ta-TiO₂ and Rh-SrTiO₃ particles were connected with each other, i.e., “necking growth” was
observed due to rather high calcination temperature and long calcination time (900°C for 24 h and 1000°C for 10 h). Nanometer order of Pt on Cr,Ta-TiO2 and Ru on Rh-SrTiO3 could be observed (indicated by an arrow), and Pt sizes were larger than Ru the reason for which is not clear. From these observations, we also confirmed the deposition of Pt and Ru cocatalysts on Cr,Ta-TiO2 and Rh-SrTiO3, respectively.

3.2. Half Reactions of Water-Splitting

We examined the evolution of H2 and O2 by Ru/Rh-SrTiO3 and Pt/Cr,Ta-TiO2 in the presence of I− and IO3− as sacrificial agents, respectively, under irradiation with visible light (420-nm LED) as shown in Figure 6. H2 evolution proceeded over Ru/Rh-SrTiO3 in the presence of I−. According to our previous paper [19], only the negligibly small amount of H2 was observed over bare Rh-SrTiO3 in the presence of I−. Thus, we concluded that in the case of Rh-SrTiO3, the cocatalyst Ru on Rh-SrTiO3 was considered as the active site for H2 evolution. O2 evolution was detected for Pt/Cr,Ta-TiO2 in the presence of IO3−. Figure 6 also includes the O2 evolution in the presence of Pt/Ti0.982Cr0.009Ta0.009O2 quoted from our paper [20]. We could enhance the O2 evolution by changing the amounts of Cr and Ta at Ti. The present Cr,Ta-TiO2 (Ti0.986Cr0.007Ta0.007O2) is the optimized composition for H2 evolution for now.

3.3. Two-Step Overall Water Splitting

We next examined water-splitting by the Ru/Rh-SrTiO3 and Pt/Cr,Ta-TiO2 photocatalysts under visible-light irradiation (420-nm LED) for ~350 h in the presence of IO3− (I/I−) as a redox mediator (Figure 7). As shown in Figure 7 in the first cycle, H2 and O2 evolutions were initially suppressed, but then increased. In contrast, in the second and third cycles, such an induction period for H2 and O2 evolutions was not observed. Although the reason for the delay in the evolutions was unclear, such phenomenon is frequently encountered. It may be due to the surface restructuring of the photocatalysts and/or cocatalysts, or due to the consumptions of holes and electrons for the residual contaminants on the surfaces of the photocatalysts and remaining oxygen in aqueous solution, respectively. In the third cycle, water-splitting activity decreased likely due to the...
Figure 6. Time courses of H₂ and O₂ evolution resulting from the half reaction of water by Ru/Rh-SrTiO₃ and Pt/Cr,Ta-TiO₂ photocatalysts irradiated with visible light (420-nm LED) in the presence of I⁻ and IO₃⁻, respectively. O₂ evolution was also included over Pt/Ti₀.₉₈₂Cr₀.₀₀₉Ta₀.₀₀₉O₂ irradiated with 420-nm LED light in the presence of IO₃⁻. The data were replotted from ref. [20].

Figure 7. Time courses of H₂ and O₂ evolution resulting from photocatalytic overall water-splitting by Ru/Rh-SrTiO₃ and Pt/Cr,Ta-TiO₂ photocatalysts under irradiation with visible light (420-nm LED). The reaction was allowed to proceed for ~350 h with twice evacuations of the system. Those by Pt/Ti₀.₉₆Cr₀.₀₂Ta₀.₀₂O₂ and Pt/Ti₀.₉₈₂Cr₀.₀₀₉Ta₀.₀₀₉O₂ under 420-nm LED light were also included in the 3rd cycle. The data were replotted from ref. [20].

detachment of cocatalysts. In addition, the amount of water decreased and the partial sample powders attached to the inner wall of the reaction vessel as the repeating cycle increased. These are possible reasons for the decrement in the water-splitting activity in the third cycle. However, H₂ to O₂ were evolved in nearly stoichiometric (~2 to 1) amounts during each irradiation cycle.

It is well-known that the electron-and-hole transfers between the redox mediators needed for the two-step system and two types of photocatalysts are not efficient. In addition, the redox mediators usually give undesirable effects, e.g., backward reactions to form water from evolved H₂ and O₂. However, the H₂ and O₂ generation rates form the overall water-splitting reaction (0.17 and 0.09 µmol h⁻¹, respectively, in the second cycle) were more than one-half of those from the half reaction of water-splitting (0.29 and 0.16 µmol h⁻¹ for H₂ and O₂ rates, respectively, in Figure 6). To our knowledge, the efficiency of H₂ and O₂ generations from the overall water-splitting is rather high. The reason is still unclear; however, an affinity between photocatalysts and the redox mediators in the constructed system would be suitable because it actually limits those combinations.
As determined by XRF analysis, the Ru/Rh-SrTiO$_3$ sample contained Ru at a molar percentage of $1 \times 10^{-2}$ (1 mol%). Therefore, because a total of 10 mg of Ru/Rh-SrTiO$_3$ was used in the water-splitting experiment as the H$_2$-photocatalyst, the amount of Ru was $5 \times 10^{-1}$ µmol. As the total amount of H$_2$ generated during the 350-h experiment was 53 µmol, we estimated that the turnover number, the ratio of total amount of produced to H$_2$ to that of Ru co-catalyst, was ~100, which exceeded 1, indicating that this reaction proceeded catalytically. These results demonstrate that the photocatalytic overall water-splitting was achieved in this system. The possible mechanism for the overall water splitting by Pt/Cr,Ta-TiO$_2$ and Ru/Rh-SrTiO$_3$ is schematically illustrated in Figure 8. Visible light-excited electrons in the conduction band of Rh-SrTiO$_3$ are thought to reduce H$_2$O and generate H$_2$ and holes in the valence band of Cr,Ta-TiO$_2$ oxidize H$_2$O and produce O$_2$. In contrast, visible-light-excited holes in the VB of Rh-SrTiO$_3$ and electrons in the isolated Cr 3d state contribute to the turnover of I$^-$/IO$_3^-$, respectively, and vice versa [19] [20].

When we compare our previous system (Pt/Ti$_{0.96}$Cr$_{0.02}$Ta$_{0.02}$O$_2$ and Pt/Ti$_{0.982}$Cr$_{0.009}$Ta$_{0.009}$O$_2$ [20]) as indicated in the third cycle in Figure 7, the H$_2$ and O$_2$ generation rates achieved ~100 times higher in the present system, constructed by Ru/Rh-SrTiO$_3$ and Pt/Cr,Ta-TiO$_2$. It is plausible that the composition of Cr,Ta-TiO$_2$ (Ti$_{0.986}$Cr$_{0.007}$Ta$_{0.007}$O$_2$) was optimized as the O$_2$-photocatalyst and that the effective Ru/Rh-SrTiO$_3$ was utilized as the H$_2$-photocatalyst. In addition, the commercial P-25 TiO$_2$ (Degussa) and famous nitrogen-doped TiO$_2$ could evolve only a trace amount of H$_2$ under the identical 420-nm LED (data not shown) and could not achieve the overall water-splitting. So the present system would be one of the candidates for obtaining H$_2$ as it consists of environmental-friendly elements.

4. Conclusions

We established a two-step overall water-splitting system that is sensitive to visible light by utilizing TiO$_2$-based and SrTiO$_3$-based photocatalysts that simulta-
neously evolve H$_2$ and O$_2$ at a molar ratio of ~2 to 1 efficiently in the presence of IO$_3^−$ (I$^−$). However, it is necessary to further enhance the visible light sensitivity. This will require the preparation of these TiO$_2$- and SrTiO$_3$-based photocatalysts which are deficient-free, more highly crystallized, and smaller-sized particles. As is known, TiO$_2$-based photocatalysts are attractive. So, we are now optimizing the types of dopants and concentrations to further enhance the visible-light sensitivity of TiO$_2$-based photocatalysts. Moreover, we have recently developed a solid-state two-step overall water-splitting photocatalyst, in which the H$_2$- and O$_2$-evolution photocatalysts were connected via silver. In this system, distilled water could be split without a redox mediator. The construction of solid-state systems using TiO$_2$-based and SrTiO$_3$-based photocatalysts in the present study may be advantageous for industrial and practical applications, as no chemicals are required as redox mediators.

References


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