Rate of Ag Photodeposition on Sr-doped NaTaO₃ Photocatalysts as Controlled by Doping Sites

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In this study, the photodeposition of metallic silver was examined by immersing strontium-doped sodium tantalate photocatalysts in aqueous AgNO₃ solution. When Ta⁵⁺ was doped with Sr²⁺ through a solid-state reaction, the observed photodeposition rate was enhanced by five times relative to that exhibited by undoped NaTaO₃. This enhancement was possibly due to restricted electron-hole recombination caused by the doping. On the other hand, when Na⁺ was doped with Sr²⁺ through a hydrothermal reaction, only slight enhancement in the photodeposition rate was observed.

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I. INTRODUCTION

The photocatalytic splitting reaction of water is a promising process for the production of hydrogen fuel. NaTaO₃ with perovskite structure doped with alkaline-earth metal elements [1, 2] or lanthanum [3] exhibits the highest quantum efficiencies for water splitting. To facilitate further development of photocatalysts, it is thus imperative to understand the mechanisms that lead to increased reaction rate caused by doping with foreign metals. As reported in our latest study of Sr-doped NaTaO₃ [4], tuning of doping sites is essential to restricting the recombination of photoexcited electrons and holes. When NaTaO₃ was doped with Sr²⁺ cations through a solid-state method (SSM), solid solutions of NaTaO₃-SrSr_{1/3}Ta_{2/3}O₃ with a Sr-rich shell covering a Sr-poor core were observed. The steady-state population of electrons excited by ultraviolet (UV) radiation was enhanced by 180 times at most in the solid-solution photocatalysts in which both A and B sites of the perovskite-structured NaTaO₃ lattice were doped with Sr²⁺. On the other hand, when the A sites were selectively doped with the same cation through a hydrothermal method (HTM), no enhancement was observed in the electron population.

In the present study, the enhancement of the photocatalytic reaction rate induced by Sr was examined by using a test reaction, namely, Ag photodeposition in a AgNO₃ solution. According to Nishimoto *et al.* [5], the photoinduced stoichiometric reaction is assumed to be

where the rate of Ag metal deposition is proportional to the rate of O₂ evolution, which is the oxidative half-reaction of water splitting.

II. EXPERIMENTAL

Strontium-doped NaTaO₃ photocatalysts were prepared by two methods: SSM and HTM. In SSM, a mixture of Na₂CO₃ (99.8%, Kanto Chemical), Ta₂O₅ (99.99%, Rare Metallic), and SrCO₃ (99.9%, Kanto Chemical) was calcined at 1173 K for 1 h and then at 1423 K for 10 h. The Na/Ta molar ratio in the mixture was adjusted to 1.05 to compensate for the loss of Na during calcination. In HTR, a 4 mol l⁻¹ aqueous solution of NaOH (96%, Wako Pure Chemical) containing Ta₂O₅ and SrCO₃ was kept at 433 K for 24 h in an autoclave (OMLab-Tech, MR28). The starting solutions had a Na/Ta molar ratio of 4. Four photocatalysts were synthesized, namely, NaTaO₃ and Sr-doped NaTaO₃ prepared by SSM, as well as NaTaO₃ and Sr-doped NaTaO₃ prepared by HTM. Hereafter, they are referred to as NTO (SSM), Sr-NTO (SSM), NTO (HTM), and Sr-NTO (HTM), respectively. Details of the preparation and characterization of these photocatalysts are reported elsewhere [4]. As determined by energy-dispersive X-ray fluorescence, the Sr concentrations relative to Ta concentrations in Sr-NTO (SSM) and Sr-NTO (HTM) were 1.8 and 2.1 mol%, respectively. UV-visible diffuse-reflection spectra of the photocatalysts were recorded by using a spectrometer (Jasco, V-570) with an integration sphere.

Prior to irradiation, a 0.5 g sample of each photocatalyst was agitated in 50 mL of AgNO₃ solution (50 mM, Junsei Chemical) for 20 h by using a magnetic stirrer. Next, the agitated mixture was irradiated with the full-spectrum light of a Hg-Xe lamp (San-ei Electric, UVS-204S). Light power at wavelengths of ≤370 nm during full-spectrum irradiation was 0.3 W. After irradiation was completed within a specific period, a small amount of photocatalyst was collected and then washed with water. Finally, the silver content of the washed photocatalyst was determined by using an X-ray fluorescence spectrometer (Shimadzu, EDX-720). The amount of photodeposited Ag was defined as the increment of Ag fraction induced by UV radiation per 0.5 g of photocatalyst, as Ag⁺ was adsorbed on the photocatalyst even in the dark. Immersion of the photocatalysts in the solution in the dark was

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FIG. 1. Sr-NTO (HTM) photocatalyst (a) as-prepared, (b) suspended for 20 h in the dark, and (c) subjected to UV radiation for 2 h in AgNO_3 solution.

FIG. 2. Sr-NTO (SSM) photocatalyst (a) as-prepared, (b) suspended for 20 h in the dark, and (c) subjected to UV radiation for 2 h in AgNO_3 solution.

essential to ensure the saturation of cation adsorption.

III. RESULTS AND DISCUSSION

The colors of NTO (HTM) and Sr-NTO (HTM) changed to brownish yellow when they were suspended in the solution in the absence of UV radiation. Figure 1 shows images of as-prepared Sr-NTO (HTM), Sr-NTO (HTM) suspended in the dark, and Sr-NTO (HTM) irradiated in solution. The brownish yellow color is attributed to adsorption of Ag^+ on the HTM-prepared photocatalysts. Meanwhile, silver oxide (Ag_2O) is known to be brown. NTO (HTM) and Sr-NTO (HTM) became dark or black upon UV radiation, indicating metal deposition.

FIG. 3. Diffuse-reflection spectra of as-prepared Sr-NTO (SSM) and Sr-NTO (HTM) and of the catalysts suspended for 20 h in AgNO_3 solution in the absence of UV radiation. The apparent absorbance without Kubelka–Munk transformation is shown.

FIG. 4. Amount of Ag deposited on the photocatalysts (a) NTO (SSM), (b) Sr-NTO (SSM), (c) NTO (HTM), and (d) Sr-NTO (HTM) as a function of irradiation time.

On the other hand, NTO (SSM) and Sr-NTO (SSM) remained white after immersion in the AgNO_3 solution, as shown in Fig. 2. The unchanged color probably resulted from the weak adsorption of Ag^+ on the SSM-prepared photocatalysts. Sr-NTO (HTM) presented perfectly cubic particles truncated with (100) surfaces, whereas Sr-NTO (SSM) exhibited a Sr-rich NaTaO_3 – $\text{SrSr}_{1/3}\text{Ta}_{2/3}\text{O}_3$ solid-solution shell. The photocatalysts prepared through the two methods exhibited different adsorption affinities for Ag^+ .

Figure 3 shows diffuse-reflection spectra of as-prepared Sr-NTO (SSM) and Sr-NTO (HTM) and of the catalysts suspended in AgNO_3 solution. The absorption edge of the two as-prepared photocatalysts was approximately 300 nm. After suspension of these photocatalysts in solution, an additional absorption was observed at longer wavelengths. The weak but finite absorption in the range of 400–500 nm caused the brownish yellow color of Sr-NTO (HTM). Weaker absorption at 300–400 nm was observed with Sr-NTO (SSM).

As shown in Fig. 4, the amount of photodeposited Ag that was determined increased linearly with irradiation time. The slope of the linear plot denotes the deposition rate on each photocatalyst. Sr-NTO (SSM) produced the highest rate among the four photocatalysts. Doping NTO with Sr^{2+} by SSM enhanced the deposition rate by five times, whereas that with Sr^{2+} by HTM resulted in an enhancement by only two times.

A more significant enhancement of the rate that is attributed to restriction of electron–hole recombination was observed with the Sr-doped catalyst prepared through SSM. Infrared absorption induced by band-gap excitation provides a quantitative measure of the excited electrons that are still separated in semiconductor photocatalysts such as NaTaO_3 [6–8] and TiO_2 [9–13]. In our earlier study [4], the four photocatalysts were excited in vacuum by using a Hg–Xe lamp, and the steady-state electron population was quantified by electron-induced infrared light absorption. The integrated absorbance of NTO doped with 1.8 mol% Sr through SSM was enhanced by 180 times [4]. The steady-state population of excited electrons was also enhanced by the same extent. The number of electrons was proportional to the integrated absorbance, while the absorption cross section per elec-

tron was not known. On the other hand, doping with 2.1 mol% Sr by HTM enhanced the integrated absorbance relative to the electron population in NTO (HTM) by only 1.8 times. The positive relation of the Ag deposition rate and excited electron population is consistent with the simple conclusion that greater numbers of excited charge carriers form more products. The apparent quantum yield of deposition was in the order of 1%.

To achieve high quantum efficiency, visible-light harvesting, and reduced cost of photocatalyst preparation, chemical modifications of NaTaO₃ photocatalyst have been intensively studied [14]. Most of the reported studies have focused on the concentration and choice of elements to be added. On the other hand, the present study demonstrates that the choice of element is not the only factor that determines the success of metal doping: the tuning of doping sites is also essential to the enhancement of reaction rate over the NaTaO₃ photocatalysts.

IV. CONCLUSION

The rate of Ag photodeposition on Sr-doped NaTaO₃ prepared through SSM and HTM was examined. Doping Ta⁵⁺ with 1.8 mol% Sr²⁺ by SSM enhanced the deposition rate by five times. On the other hand, doping Na⁺ with Sr²⁺ at nearly the same concentration by HTM enhanced the rate by only two times. The pronounced rate enhancement over the photocatalyst prepared by SSM is attributed to the restriction of electron-hole recombination caused by doping of Ta⁵⁺.

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