

Formation of Surface Nano-step Structures and Improvement of Photocatalytic Activities of NaTaO₃ by Doping of Alkaline Earth Metal Ions

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Powders of NaTaO₃ doped with alkaline earth metal ions were prepared. Scanning electron microscopy observation revealed that NaTaO₃ crystals doped with Ca, Sr, and Ba became smaller than nondoped NaTaO₃ crystals. In addition, nano-step structures were constructed on the surfaces of NaTaO₃ doped with Ca, Sr, and Ba. The photocatalytic activity of water splitting on NaTaO₃ was improved by the doping of Ca, Sr, and Ba. It is due to the small particle size and the formation of surface nano-step structures as observed for La doping.

Photocatalytic water splitting into H₂ and O₂ is an attractive theme from the viewpoint of the production of H₂ which is an ultimately clean energy. It has been reported that some oxides are highly active photocatalysts for water splitting under UV irradiation.¹⁻⁹ Especially, there are many reports about highly efficient water splitting using tantalate photocatalysts.^{2-4,7-9} In particular, NaTaO₃ doped with La is the most active photocatalyst: the apparent quantum yield is 56% at 270 nm.³ In this case, well-crystallized fine particles with surface nano-step structures are obtained by doping of La ions. Reduction sites are effectively separated from oxidation sites at the nano-step structure. In addition, NiO cocatalysts which are loaded as ultra fine particles work as highly efficient active sites for H₂ formation. Thus, the control of particle sizes and surface morphology can be regarded as one of the strategies to improve the photocatalytic performance. In the present study, effects of doping of alkaline earth metal ions on the surface morphology and the photocatalytic activity of NaTaO₃ are investigated.

Powders of NaTaO₃ doped with 2 mol % of alkaline earth metal ions Mg, Ca, Sr, and Ba (denoted as NaTaO₃:A hereafter) were prepared by a solid-state reaction. Starting materials, Na₂CO₃ (Kanto Chemical; 99.5%), Ta₂O₅ (Rare metallic; 99.99%), MgO (Kanto Chemical; 99%), CaCO₃ (Kanto Chemical; 99%), SrCO₃ (Kanto Chemical; 99.9%), and BaCO₃ (Kanto Chemical; 99%) were mixed in the ratio of Na:A:Ta = 1.05:0.02:1. The excess amount of sodium was added in the starting mixture to compensate the volatilization. The mixtures were calcined in air at 1173 K for 1 h and then 1423 K for 10 h in a platinum crucible. The excess sodium was washed out with water after the calcination. The obtained powder was confirmed by X-ray diffraction (Rigaku; MiniFlex). A NiO cocatalyst was loaded by an impregnation method from an aqueous solution of Ni(NO₃)₂·6H₂O (Wako Pure Chemical; 98%).

Photocatalytic reactions were carried out in a gas-closed circulation system. The catalyst powder (0.5 g) was dispersed in pure water (350 mL) using a magnetic stirrer. The light source was a 400-W high-pressure mercury lamp (SEN; HL400EH-5). The amounts of evolved H₂ and O₂ were determined using

gas chromatography (Shimadzu, GC-8A). Diffuse reflection spectra were obtained using a UV-vis-NIR spectrometer (JASCO; Ubest-570) and were converted from reflectance to absorbance by the Kubelka-Munk method. Surface areas were determined by BET measurement (Coulter; SA3100). The catalysts were observed using scanning electron microscopes (Hitachi; S-5000 and Jeol; JSM-6700F).

X-ray diffraction patterns of NaTaO₃:A were the same as that of NaTaO₃. However, shifts in the peak position were observed for NaTaO₃:A except for NaTaO₃:Mg, indicating that alkaline earth metal ions were homogeneously doped into the NaTaO₃ lattice. It was found from SEM observation that particle sizes of NaTaO₃:A (A = Ca, Sr, and Ba) (0.1–0.5 μm) became smaller than that of nondoped NaTaO₃ (2–3 μm). In addition, many nano-step structures were constructed on their surfaces. Figure 1 shows a SEM photograph of NaTaO₃:Sr as the representation. The increases in surface areas were observed for the cases of Ca, Sr, and Ba doping. The morphology of NaTaO₃ crystals doped with alkaline earth metal ions was quite similar to that of La doping.³ Thus, it was revealed that fine crystals of NaTaO₃ with nano-step structures also were able to be obtained by doping of alkaline earth metal ions. However, the variation of morphology was not observed for Mg doping. Ca²⁺, Sr²⁺, and Ba²⁺ ions have suitable sizes to occupy the A site in the perovskite structures; Ca²⁺: 1.48 Å, Sr²⁺: 1.58 Å, Ba²⁺: 1.75 Å, and Na⁺: 1.53 Å.¹⁰ Therefore, local structures were distorted and crystal growths were inhibited. In contrast, the size of a Mg²⁺ ion (1.03 Å, 8 coordination) is much smaller than that of a Na⁺ ion, implying the difficulty of substitution of Mg²⁺ ions for Na⁺ ions. Thus, there is the relationship between the formation of fine crystals and the size of a doping ion. These morphology changes seem to occur when a cation with a similar ionic radius to Na⁺ and higher valency than Na⁺ is replaced for an A site in a perovskite lattice.

Table 1 shows photocatalytic activities of NaTaO₃ doped with alkaline earth metal ions for water splitting. Band gaps of

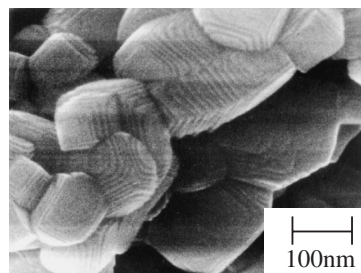


Figure 1. Scanning electron microscope photograph of NaTaO₃:Sr (2%).

Table 1. Photocatalytic water splitting into H₂ and O₂ over NaTaO₃ doped with alkaline earth metal ions

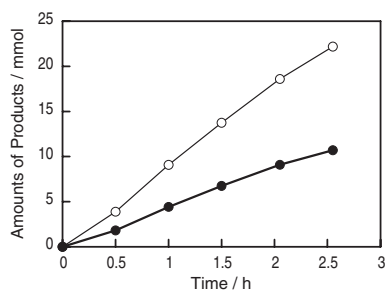
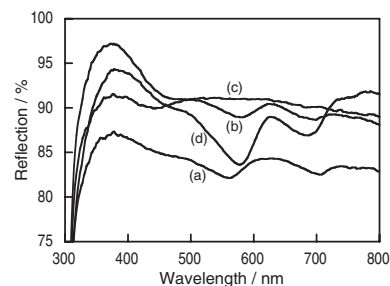
Dopant	Particle Size/ μm	Surface Area/ m^2g^{-1}	NiO loaded /wt %	Activity/ $\mu\text{mol h}^{-1}$	
				H ₂	O ₂
None	2–4	0.3	0	157	60
			0.05	1670	782
Mg(2%)	2–8	0.5	0	121	55
			0.1	985	456
Ca(2%)	0.1–0.5	2.6	0	204	91
			0.2	4910	2370
Sr(2%)	0.1–0.3	3.4	0	530	255
			0.2	9500	4700
Ba(2%)	0.1–0.3	3.5	0	529	232
			0.2	9300	4690

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

NaTaO₃:A (A = Ca, Sr, and Ba) (4.1 eV) were slightly wider than that of nondoped NaTaO₃ (4.0 eV). The photocatalytic activities of NaTaO₃ without NiO cocatalysts were increased when Ca, Sr, and Ba were doped. The activities of NaTaO₃:A (A = Sr and Ba) were higher than that of NaTaO₃:Ca. The activities of NaTaO₃:A (A = Ca, Sr, and Ba) were increased by 20 times when NiO cocatalysts were loaded. In contrast, those of nondoped NaTaO₃ and NaTaO₃:Mg were increased by 10 times. Thus, the loading effect of NiO cocatalysts on activities for NaTaO₃:A (A = Ca, Sr, and Ba) with fine crystal sizes and the step structures was more remarkable than that for NaTaO₃ and NaTaO₃:Mg.

The NiO(0.2 wt %)-loaded NaTaO₃:Sr (2%) showed the high photocatalytic activity for water splitting into H₂ and O₂ as shown in Figure 2. The rates of H₂ and O₂ evolution were 9.5 and 4.7 mmol h⁻¹, respectively. The babbling of gas evolution was actually observed during water splitting on the NiO-loaded NaTaO₃:A (A = Ca and Sr) photocatalysts. The activity of this photocatalyst was about half as high as that of NiO-loaded NaTaO₃:La. However, the activity was considerably higher than those of other reported photocatalysts.^{1,2,4,9} The difference in the activity between Sr²⁺ and La³⁺ doping seems to be due to the difference in the valency and the doping site. Sr²⁺ was homogeneously doped in the NaTaO₃ lattice while a large part of La³⁺ was doped near the surface.

Figure 3 shows diffuse reflection spectra of NaTaO₃:A (A = Ca, Sr, Ba, and La). Two characteristic absorption bands around

**Figure 2.** Photocatalytic water splitting into H₂ and O₂ over NiO(0.2 wt %)/ NaTaO₃:Sr (2%) in pure water; open circle: H₂, closed circle: O₂. Catalyst: 0.5 g, pure water: 350 mL, 400-W high-pressure Hg lamp, inner irradiation cell made of quartz.**Figure 3.** Diffuse reflection spectra of NiO(0.2 wt %)-loaded NaTaO₃ doped with (a) Ca, (b) Sr, (c) Ba, and (d) La.

580 and 690 nm due to nickel loaded were observed for NiO-loaded NaTaO₃:A (A = Ca and Sr) as well as for NiO-loaded NaTaO₃:La although the absorption bands were slightly shifted. In addition, the colors of NiO-loaded NaTaO₃:A (A = Ca and Sr) were pale pink similar to that of a NiO-loaded NaTaO₃:La. This result suggests that nickel was loaded as ultra fine particles on the nano-step surface as reported for NiO/NaTaO₃:La.³ As described above, doping of alkaline earth metal ions affected not only the morphology of crystals but also the photocatalytic activities of NaTaO₃ as well as La ions doping. The following three factors are considered for the improvement of activities. i) Charge separation was promoted by doping of Ca, Sr, and Ba because of the charge unbalance in the A site. ii) The number of electrons and holes that took part in the photocatalytic reaction was increased by decreasing the distance from the formation place of photogenerated carriers to the catalytic surface. iii) Reduction sites were separated from oxidation sites by construction of surface nano-step structures.

In conclusion, it has been found that fine NaTaO₃ crystals with nano-step structures were able to be obtained by doping of not only La ions but also alkaline earth metal ions. The improvement of the photocatalytic activities was also achieved by doping of alkaline earth metal ions. Thus, the importance of the morphology control for the improvement of the photocatalytic activity was also demonstrated in the present study.

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