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Effects of doping of metal cations on morphology, activity, and visible light response of photocatalysts

Akihiko Kudo [a,b,*], Ryo Niishiro [a], Akihide Iwase [a], Hideki Kato [a]

[a] Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
[b] Core Research Evolutional Science and Technology, Japan Science and Technology Agency (CREST/JST), Japan

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Abstract

Effects of doping of metal cations into wide band gap semiconductor photocatalysts on morphology, visible light response, and photocatalytic performance were studied. Doping of lanthanide and alkaline earth ions improved activity of a $NaTaO_3$ photocatalyst for water splitting. Lanthanum was the most effective dopant. The $NaTaO_3$:La with a NiO cocatalyst gave 56% of a quantum yield at 270 nm. This remarkable photocatalytic activity was brought by formations of nano-crystalline particle and surface nano-step structure by the doping. On the other hand, metal cation doping into ZnS, TiO_2, and $SrTiO_3$ gave visible light responses for H_2 or O_2 evolution from aqueous solutions containing of sacrificial reagents. The visible light responses were due to the electronic transition from donor levels formed with dopants to conduction bands of the host photocatalysts. Codoping was effective to compensate charge unbalance brought by doping of transition metal cations, resulting in the improvement of visible light response for photocatalytic reactions. Among the transition metal-doped photocatalysts, $SrTiO_3$ doped with Rh ($SrTiO_3$:Rh) was the novel metal oxide photocatalyst that produced H_2 under visible light irradiation. The $SrTiO_3$:Rh photocatalyst was employed with O_2 evolution photocatalysts such as $BiVO_4$ and WO_3 for construction of Z-scheme systems that were active for water splitting into H_2 and O_2 under visible light irradiation.

Keywords: Photocatalyst; Hydrogen; Doping; Oxide; Sulfide; Nanostructure; Visible light response

1. Introduction

Photon energy conversion reactions using semiconductor electrodes [1–7] and powdered photocatalysts [8–25] have been extensively studied since the Honda–Fujishima effect [26] was reported. Efficient water splitting into H_2 and O_2 using a powdered photocatalyst is attractive because it can be a clean and simple process for H_2 production using a natural energy. Water splitting utilizing solar light, that is called "solar hydrogen production", is the final target in the present research field.

Many metal oxide photocatalysts have been reported for water splitting so far. The present authors have found many niobate and tantalate photocatalysts [19,20,25]. Some metal oxide photocatalysts such as $NaTaO_3$ show high activities for water splitting although they work only under UV irradiation because of their wide band gaps. Domen and coworkers have reported water splitting using metal (oxy)nitride photocatalysts that are nonoxide materials [21,23,24]. Water splitting under visible light irradiation has been achieved by some photocatalyst systems [16,18,21,24]. However, the efficiencies are not satisfying. Development of new photocatalyst materials is still an important topic.

Photocatalytic activities are affected by particle size, crystallinity, surface properties, etc. These factors are controlled by changes in a preparation method, loading of a cocatalyst, and introducing a foreign element. Doping of

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* Corresponding author. Address: Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. Tel.: +81 35228 8267; fax: +81 35261 4631.
E-mail address: a-kudo@rs.kagu.tus.ac.jp (A. Kudo).

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a foreign element into a photocatalyst is one of the strategies that can affect the morphology (particle size and surface structure) of photocatalyst particles. On the other hand, doping of transition metal cations into photocatalysts with wide band gaps such as TiO_2 and $SrTiO_3$ has been studied for a long time in the research field of photoelectrochemistry and photocatalysis in order to modify electronic structure and develop materials with visible light responses [27–34]. However, doping is regarded as an unsuitable method because photocatalytic efficiencies drastically decrease in many cases, even if visible light absorption bands are obtained. Recently, anion doping of nitrogen, sulfur, and carbon has been extensively investigated [35–38].

The present review paper introduces the improvement of the activity of a $NaTaO_3$ photocatalyst by doping lanthanum and alkaline earth metals. Development of visible light-driven photocatalysts by doping of metal ions into ZnS, TiO_2, and $SrTiO_3$ of wide band gap semiconductor photocatalysts is also reported. In the present paper, doping means the substitution of dopants for metal cations of the host materials at crystal lattice points. The amounts of dopants are quite large (0.1–4%).

2. Highly efficient water splitting using NiO-loaded $NaTaO_3$ photocatalysts doped with lanthanum and alkaline earth metal ions [39,40]

$NaTaO_3$ loaded with a NiO cocatalyst is a highly active photocatalyst for water splitting [41]. In general, photocatalytic activities are increased when the particle size becomes small and highly crystalline [42–44]. Therefore, the authors tried to reduce the particle size of the $NaTaO_3$ photocatalyst by doping. Fig. 1 shows SEM photographs of nondoped and La-doped $NaTaO_3$. The particle size of La-doped $NaTaO_3$ was 0.1–0.7 μm while that of nondoped $NaTaO_3$ was 2–3 μm. The particle sizes of $NaTaO_3$ also became small by doping of Ca, Sr, and Ba. The surface of nondoped $NaTaO_3$ was smooth whereas La-doped $NaTaO_3$ particles had surface nanostructure with steps of 3–15 nm. It was also observed for Ca-, Sr-, and Ba-doped $NaTaO_3$. Thus, the doping of La, Ca, Sr, and Ba affected the morphology of the $NaTaO_3$ particle. This effect was due to the difference in ionic radii between dopants and Na cation [45]. Ionic radii of La^{3+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} are 1.50, 1.48, 1.58, and 1.75 Å in 12-coordination, respectively. Those values are similar to an ionic radius of Na^+ (1.53 Å). On the other hand, in six-coordination, ionic radii of La^{3+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} are 1.17, 1.14, 1.32, and 1.49 Å, respectively. Those values are smaller than the ionic radius of Ta^{5+} (0.78 Å). Therefore, Na in $NaTaO_3$, an A site in perovskite structure, is replaced with those dopants. Crystalline and fine particles, and surface nanostep structure were formed by suppression of crystal growth due to distortion of local structure. These effects were not observed for Mg-doping.

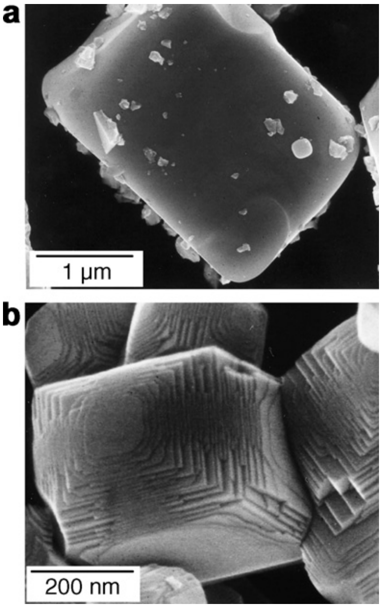

Fig. 1. Scanning electron microscope images of (a) nondoped $NaTaO_3$ and (b) La-doped $NaTaO_3$.

Table 1 shows photocatalytic activities for water splitting on La-, Ca-, Sr-, and Ba-doped $NaTaO_3$. The activity of $NaTaO_3$ was increased by La-, Ca-, Sr-, and Ba-doping and was drastically improved by NiO-loading. The NiO cocatalyst works as a H_2 evolution site. La-doped $NaTaO_3$ with the NiO cocatalyst showed the highest activity. The apparent quantum yield of this photocatalyst was 56% at 270 nm. Vigorous evolution of bubbles of H_2 and O_2 was observed using a 200-W Xe–Hg lamp.

Table 2 shows H_2 or O_2 evolution from aqueous solutions containing of sacrificial reagents on La-, Ca-, Sr-, and Ba-doped $NaTaO_3$ photocatalysts. The photocatalytic activities of the H_2 and O_2 evolution were increased 1.2–1.3 and 3–4 times by doping, respectively. This result suggests that the doping mainly affects the formation of O_2 evolution sites.

Table 1
Photocatalytic water splitting into H_2 and O_2 over $NaTaO_3$ doped with La and alkaline earth metal ions

Dopant	BG (eV)	Particle size (μm)	SA (m^2g^{-1})	NiO-loaded (wt%)	Activity ($mmol\ h^{-1}$)	
					H_2	O_2
None	4.0	2–4	0.3	0	0.16	0.06
				0.05	1.67	0.78
Mg(2%)	4.0	2–8	0.5	0	0.12	0.06
				0.1	0.99	0.46
Ca(2%)	4.1	0.1–0.5	2.6	0	0.20	0.09
				0.2	4.91	2.37
Sr(2%)	4.1	0.1–0.3	3.4	0	0.53	0.26
				0.2	9.50	4.70
Ba(2%)	4.1	0.1–0.3	3.5	0	0.53	0.23
				0.2	9.3	4.69
La(2%)	4.1	0.1–0.7	3.2	0	0.45	0.21
				0.2	19.8	9.66

Catalyst: 0.5–1 g, pure water: 350–390 mL, 400-W high-pressure Hg lamp, inner irradiation cell made of quartz.