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Effects of Nitrogen Doping on Photocatalytic Water-splitting Activity of Pt/$KTa_{0.92}Zr_{0.08}O_3$ Perovskite Oxide Catalyst

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Effects of N doping in $KTa(Zr)O_3$ on the photocatalytic activity under visible light irradiation were investigated and it was found that Pt-loaded $K_{0.93}Ta_{0.92}Zr_{0.08}O_{2.79}N_{0.21}$ photocatalyst achieved a complete splitting of water under 420 nm cut-off conditions.

Photocatalytic splitting of H_2O into H_2 and O_2 has an advantage as a simple method for solar energy conversion to a useful chemical compound, hydrogen, which is regarded as an environmentally compatible energy carrier. For the purpose of utilizing solar energy for hydrogen production, development of visible light-driven photocatalysts with high catalytic activity is highly desirable. There are several methods for modifying the photoabsorption properties of oxide semiconductors, and cation doping has been commonly performed for improving the photocatalytic activity in visible light.[1–3] In contrast, it was found recently that anion doping, in particular, N doping, is effective for improving visible light response of TiO_2.[4–6] In our previous study, it was found that the photocatalytic activity of $KTaO_3$ ($E_g = 3.6$ eV) was improved by doping Zr^{4+} ion to Ta sites.[7] Although absorption spectra were not changed, doped Zr works as an acceptor resulting in decrease in the electron concentration in $KTaO_3$ and improvement of electron mobility which may lead to the improvement of photocatalytic activity. In this study, effects of N doping on the photoabsorption properties and the photocatalytic activity of $KTa(Zr)O_3$ to H_2O splitting were investigated. Although ZrO_2–TaON solid solution has been reported as photocatalyst for H_2 evolution,[8] the complete photocatalytic decomposition of H_2O into H_2 and O_2 under visible light irradiation was achieved in this study.

Details of the preparation of Zr-doped $KTaO_3$ were described in our previous report.[9] Obtained $KTaO_3$ powder was calcined in NH_3 gas flow (75 mL min^{-1}) for 12 h. Loading Pt cocatalysts onto the N-doped $KTaO_3$ powder was performed by impregnation with aqueous $Pt(NH_3)_4(NO_3)_2$ (Sigma-Aldrich Co.) solution followed by thermal treatment at 523 K. The photocatalytic decomposition of water was performed with a closed circulating system. The catalyst powder (50 mg) was suspended in 80 mL of pure water. The quartz reaction cell was irradiated by a 300 W Xenon lamp (ILC technology Inc., Cermax LX-300F) external light source with glass filter. The amounts of H_2 and O_2 formed were measured by gas chromatograph with a thermal conductivity detector (Shimadzu Corp., GC-8A), which was connected to a conventional volumetric circulating line with a vacuum pump.

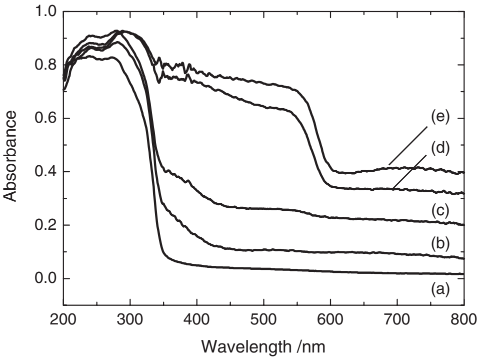

Figure 1. UV–vis spectra of (a) $KTa(Zr)O_3$, N-doped $KTa(Zr)O_3$ treated at (b) 973, (c) 1073, (d) 1173, and (e) 1273 K.

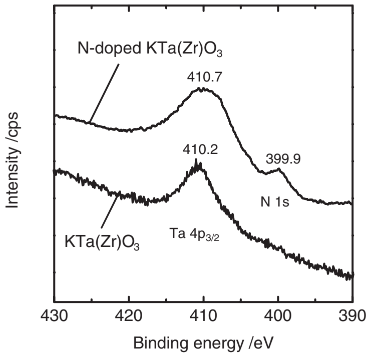

Figure 2. XPS spectra of $KTa(Zr)O_3$ and N-doped $KTa(Zr)O_3$.

Figure 1 shows UV–vis absorption spectra of $KTa(Zr)O_3$ treated with NH_3 at various temperatures. A photoabsorption peak newly appeared at 350–400 nm by introduction of nitrogen, and the baselines of spectra were also increased by reduction of the sample and formation of oxygen defects during NH_3 treatment. XPS measurement was performed for investigating the electronic states of NH_3-treated catalysts and also to confirm that nitrogen was introduced into the catalyst. In analogy to TiO_2, it is expected that the introduction of N into $KTaO_3$ is useful for improving photocatalytic activity under visible light. Figure 2 shows XPS spectra of Ta $4p_{3/2}$ after thermal treatment at 1073 K and that of nondoped $KTa(Zr)O_3$ as a reference. The binding energy was normalized by adjusting C 1s peak to be 284.6 eV. As shown in Figure 2, a new peak which can be assigned to N 1s was appeared in the XPS spectrum of N-doped $KTa(Zr)O_3$ with a higher binding energy Ta $4p_{3/2}$ peak. In this catalyst, surface N/Ta ratio was estimated to be 0.43 from the peak areas of Ta $4p_{3/2}$ and N 1s peaks. The absorption peaks at 350–400 nm in UV–vis spectra can be assigned to the excitation from doped N level to conduction band. Absorbance at 350–600 nm in N-doped $KTa(Zr)O_3$ increased with increasing the heat treatment temperature with NH_3. In N-doped $KTa(Zr)O_3$

Table 1. Photocatalytic activity for water splitting on Pt-loaded $KTa(M)O_{2.79}N_{0.21}$[a]

Dopant (M)	Specific surface area/$m^2\,g^{-1}$	Formation rate/$\mu mol\,g_{cat}^{-1}\,h^{-1}$	
		H_2	O_2
Zr	3.4	53.8	24.5
Hf	3.5	26.8	2.4
None	3.3	14.0	3.5
Ti	3.2	13.0	1.7
Nb	3.1	8.5	Trace
V	3.4	0.0	0.0

[a] Catalyst: $Pt(0.2\,wt\,\%)/K_{0.95}Ta_{0.92}M_{0.08}O_{2.79}N_{0.21}$, light source: 300 W Xe lamp with cut-off filter ($\lambda > 385$ nm), pH: 7.8.

prepared at 1173 and 1273 K, diffraction peaks assigned to Ta_3N_5 were observed. Absorption edge of Ta_3N_5 has been reported at 600 nm,[10] and thus increased absorption at 350–600 nm in UV–vis spectra could be attributed to the formation of Ta_3N_5. N-Doped $KTa(Zr)O_3$ prepared at 1073 K showed the highest H_2 formation rate (Supporting Information).[12] Ta_3N_5 has low photocatalytic activity for water splitting,[11] thus optimized N-doping temperature seems to exist at 1073 K. The amount of N doped in photocatalyst treated at 1073 K was determined to be $K_{0.93}Ta_{0.92}Zr_{0.08}O_{2.79}N_{0.21}$ by using EDX.

Table 1 shows the effects of cation doping on photocatalytic activity of N-doped $KTaO_3$ for water splitting. Although the cation-doped catalysts had almost the same surface area, pentavalent metal cation (Nb^{5+}, V^{5+})- and Ti^{4+}-doped $KTaO_{2.79}N_{0.21}$ catalysts showed low photocatalytic activity. The color of these catalysts was slightly dark, and so doped Nb^{5+}, V^{5+}, and Ti^{4+} cations formed an impurity level in the band gap of $KTaO_3$. It was suggested that the formed impurity level worked as a recombination center for photogenerated charge carriers. Therefore, the formation rates of H_2 and O_2 were decreased by doping with Nb^{5+}, V^{5+}, and Ti^{4+}. On the other hand, doping with Zr^{4+} and Hf^{4+} cations effectively improved H_2 and O_2 formation rates. This tendency of cation doping is almost the same with that of nondoped $KTaO_3$ in our previous study.[7]

Among the examined cations, doping Zr gives the highest activity and so, doping Zr is also effective for N doping. In the case of $KTa(M)O_{3-x}N_x$ catalyst, it is suggested that doped nitrogen was localized near the surface because N doping was performed by calcination in NH_3 flow and effectively works for increasing the number of photoexcited electrons and holes. Doping Zr or Hf is also effective to improve the mobility of photoexcited electrons. Therefore, catalysts doped with tetravalent metal cations showed high photocatalytic activity for water splitting.

Figure 3 shows the gas formation rates on optimized $Pt/K_{0.93}Ta_{0.92}Zr_{0.08}O_{2.79}N_{0.21}$ and $Pt/K_{0.95}Ta_{0.92}Zr_{0.08}O_3$ using a Xe lamp with cut-off filter as a light source. Photocatalytic activity was obviously improved by N doping because of the improved utilization of the visible light for photocatalytic reaction. Furthermore, surface area of catalyst was slightly increased by N doping, and so one reason for increase in the reaction rate could be the increased reaction site number. Formation amounts of H_2 and O_2 were not stoichiometric because formed oxygen may be trapped on the catalyst surface and this is also reported for TiO_2. Under visible light irradiation, H_2 and O_2 formation rates were 25.3 and 13.0 $\mu mol\,g^{-1}\,h^{-1}$, respectively, without formation of N_2. In contrast, no H_2 or O_2 formation was observed on non N-doped $KTaO_3$. Therefore, it was found that the complete photocatalytic water splitting under 420 nm cut-off light irradiation condition was achieved by nitrogen doping Zr-doped $KTaO_3$.

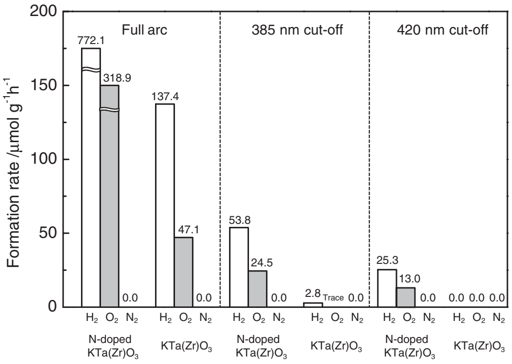

Figure 3. Wavelength dependence of photocatalytic activity on $Pt/K_{0.93}Ta_{0.92}Zr_{0.08}O_{2.79}N_{0.21}$ and $Pt/K_{0.95}Ta_{0.92}Zr_{0.08}O_3$. Pt co-catalyst: 0.2 wt %, 300 W Xe lamp with cut-off filter, pH 7.8.

Consequently, this study reveals that introduction of N into $KTa(Zr)O_3$ is effective for improving the photocatalytic activity under visible light. The optimized temperature for NH_3 treatment was determined to be 1073 K, and N-doped $KTaO_3$ catalyst achieved complete photocatalytic decomposition of H_2O into H_2 and O_2 under 420 nm cut-off.

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