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Photocatalytic splitting of water into hydrogen and oxygen on organic dye modified KTa(Zr)O₃ catalyst

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Abstract

Photocatalytic activity of KTaO₃ catalyst to water splitting is much improved by organic dye-modification. In particular, cyanocobalamin (Vitamin B₁₂) is the most effective for improving water splitting activity, and the formation rate of H₂ and O₂ are achieved values of 1912 and 979 μmol g⁻¹ h⁻¹, respectively, under the light irradiation from Xe lamp (300W). Mechanism of photocatalytic H₂O splitting into H₂ and O₂ on PtOₓ/KTa(Zr)O₃ modified with various dyes were investigated. Photoluminescence (PL) spectra of KTaO₃ catalysts suggested that the excitation energy transfers from KTaO₃ to Cr-Tetraphenylporphyrin (Cr-TPP) and PtOₓ co-catalyst. Transient response of photoexcited potential revealed that the excitation state of KTaO₃ was enlarged over 500 μs by dye-modification. Photo-excited electron in KTaO₃ transfers to dye, and a long charge separation state was achieved. Thus, it was suggested that the photocatalytic activity was much improved by increasing lifetime of photo-excited charges which can reach to the reaction site effectively.

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1. Introduction

Hydrogen production by photocatalytic water splitting with solar light has been attracting much attention from viewpoint of solar energy conversion because of the reduction of fossil fuel usage and CO₂ emission. Among the various H₂ production processes, photocatalytic splitting of H₂O into H₂ and O₂ is the simplest method for solar energy conversion. Among the various visible light driven photocatalysts, Z-scheme type photocatalyst system (two step photoexcitation) using I⁻/IO₃⁻ mediator was proposed [1]. This system imitates photosynthesis in plants, and is highly interesting from the viewpoint of artificial photosynthesis. In contrast, H₂ and O₂ can be also generated at stoichiometric ratio from water by using single excitation in GaN and ZnO solid solution [2]. Although these photocatalytic systems can form hydrogen under visible light irradiation, further improvement in their photocatalytic activity is still requested.

In the photocatalytic reaction process, photogenerated electrons and holes in the oxide semiconductor migrate to

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the surface, and redox reaction occurs on the active sites. During charge separation, photogenerated charges easily recombine in the photocatalyst particles. Relaxation processes of the excited state and the relationship between photocatalytic activity and excitation lifetime have been investigated on TiO₂ [3-5]. A good correlation exists between the excitation lifetime of charge in TiO₂ and photocatalytic reactivity; thus, prolonging the excited state of the photocatalyst is highly important for achieving a high photocatalytic activity.

In our previous study, it was found that KTa(Zr)O₃ photocatalytic activity of overall water splitting was significantly enhanced by modifying porphyrinoids [6] or phthalocyanines [7]. In this study, modification effects of various dyes were investigated on the water splitting reaction on KTa(Zr)O₃ photocatalyst for optimizing the organic dye. Furthermore, the electron transfer between KTa(Zr)O₃ and Cr-TPP was studied for understanding the charge transfer mechanism in this dye-modified KTa(Zr)O₃ photocatalyst.

2. Experimental Section

Zr-doped KTaO₃ (K₀.₉₅Ta₀.₉₂Zr₀.₀₈O₃) was prepared with a conventional solid-state reaction method by using K₂CO₃ (Wako Pure Chemical Industries, Japan, >99.5%), Ta₂O₅ (Kojundo. Chemical, Japan, 99.9%) and ZrO(NO₃)₂·2H₂O (Nacalai tesque, Japan, >95.0%) for starting materials [6]. The precursor mixture was obtained by the evaporation of an aqueous suspension of Ta₂O₅, K₂CO₃ and ZrO(NO₃)₂·6H₂O. After grinding the precursor powders in an alumina mortar with a Al₂O₃ pestle, the obtained precursor was calcined at 1173 K in air for 10 h. Crystal structure of KTa(Zr)O₃ was identified to a single phase of KTaO₃, and the change in lattice constant due to Zr⁴⁺ doping was confirmed by X-ray diffraction analysis (Rigaku Corp., RINT 2500H/PC). PtOₓ (0.2 wt%) / Dye (0.8wt%) / KTa(Zr)O₃ photocatalysts were prepared by evaporation to dryness of each commercial organic dyes and Pt source. Chromium tetraphenylporphyrin complex, Cr-TPP, was prepared by reflux with 5, 10, 15, 20-tetraphenyl-21H,23H-porphine (Sigma-Aldrich Co.) and CrCl₃ (Alfa Aesar) in an anhydrous pyridine solution for 6 h. Dye modification of Zr-doped KTaO₃ was performed by an conventional impregnation technique, i.e. the powder was suspended in dye solved pyridine and pyridine solvent was evaporated to dryness under consecutive stirring with magnetic stirrer. Finally, PtOₓ was loaded on dye with Pt(NH₃)₄(NO₃)₂ (Sigma-Aldrich Co.) aqueous solution as a co-catalyst.

Photocatalytic water splitting reaction was performed with the glass closed circulating reactor system connected to TCD type gas chromatograph (Shimadzu, GC-8A). The reaction solution which was consisted of catalyst powder (50 mg) and distilled water (30 ml, pH 11 controlled by KOH), was stirred during a photocatalytic water splitting reaction. The reaction solution was irradiated through a quartz glass window by a 300 or 500 W Xenon lamp. Before the reaction started, the absence of gas leakage was confirmed for 1 h by performing a reaction without irradiation of light, dark reaction.

3. Results and Discussion

TEM observation was performed to confirm the dispersion state of PtOₓ and organic dyes on KTa(Zr)O₃. As shown in Figure 1, KTaO₃ crystalline particles were covered with amorphous layer, which could be assigned to a
modified organic dye. In this case, the amount of dye is corresponded to 5~6 monolayer on $\text{KTa(Zr)}_3$ by assuming dense sphere of $\text{KTaO}_3$ and molecular area of TPP as $2.25 \text{ nm}^2$[8]. In addition, small PtO$_X$ particles of which diameter are ca. 5 nm are observed in amorphous dye. Therefore, the catalyst was consisted of KTa(Zr)$_3$ partially.

![Figure 2](image)

**Figure 2.** Amounts of $\text{H}_2$ and $\text{O}_2$ formed by splitting of water on the photocatalysts consisting of PtO$_X$, Cyanocobalamin and KTa(Zr)$_3$ as a function of reaction time. Light source: 500 W Xe lamp. Data plots of Dye/KTa(Zr)$_3$, PtO$_X$/KTa(Zr)$_3$ and PtO$_X$/Dye overlap on the x-axis because of low photocatalytic activity.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\text{H}_2$</th>
<th>$\text{O}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanocobalamin (VitaminB$_{12}$)</td>
<td>1912</td>
<td>979</td>
</tr>
<tr>
<td>Tetrakis(pentafluorophenyl) porphine (TPFPP)</td>
<td>1009</td>
<td>487</td>
</tr>
<tr>
<td>Cr-Tetraphenyl porphyrin (Cr-TPP)</td>
<td>908</td>
<td>471</td>
</tr>
<tr>
<td>Chlorohemin</td>
<td>867</td>
<td>381</td>
</tr>
<tr>
<td>Rohdamine 6G</td>
<td>834</td>
<td>295</td>
</tr>
<tr>
<td>Tetraphenylporphine Tetrusulfonic Acid (TPPS)</td>
<td>754</td>
<td>346</td>
</tr>
<tr>
<td>Rose Bengal</td>
<td>713</td>
<td>290</td>
</tr>
<tr>
<td>Tetrakis(4-carboxyphenyl) porphine (TCPP)</td>
<td>664</td>
<td>274</td>
</tr>
<tr>
<td>Perylene</td>
<td>549</td>
<td>264</td>
</tr>
<tr>
<td>Crystal Violet</td>
<td>527</td>
<td>166</td>
</tr>
<tr>
<td>Pentamethylene Bis[4-(10,15,20-triphenyl porphine-5-yl) benzoate]-dizinc(II) (Zn-TPP dimer)</td>
<td>522</td>
<td>223</td>
</tr>
<tr>
<td>Malachite Green</td>
<td>436</td>
<td>134</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>424</td>
<td>121</td>
</tr>
<tr>
<td>Capsanthin</td>
<td>423</td>
<td>146</td>
</tr>
<tr>
<td>Eosin Y</td>
<td>418</td>
<td>148</td>
</tr>
<tr>
<td>$\beta$-carotene</td>
<td>361</td>
<td>145</td>
</tr>
<tr>
<td>Coronene</td>
<td>227</td>
<td>97</td>
</tr>
<tr>
<td>None</td>
<td>108</td>
<td>51</td>
</tr>
</tbody>
</table>
covered with organic dye and PtOX nanoparticle dispersed on it.

Figure 2 shows the water-splitting activity of Zr-doped KTaO₃ photocatalysts. The flat-band potential of KTaO₃ vs. NHE and its band gap has been reported as -0.2 V and 3.5 eV, respectively [9]. Thus, from the band structure of KTaO₃, photocatalytic water splitting could proceed on KTaO₃. However, only small amounts of H₂ and O₂ was formed on a PtOX-loaded KTa(Zr)O₃ photocatalyst. The oxidation state of the Pt co-catalyst was Pt⁴⁺ without H₂ reduction treatment, which was confirmed from XPS measurement (the data is not shown here), and it is considered that the oxidation activity of PtOX to H₂ into H₂O is negligibly small. Therefore, the water-splitting reaction does not proceed on this catalyst because of the low efficiency of charge transfer from KTa(Zr)O₃ to PtOX. On the other hand, the water splitting activity of the KTa(Zr)O₃ photocatalyst was evidently improved by dye modification for PtOX/KTa(Zr)O₃.

Table 1 shows the water-splitting activity of KTa(Zr)O₃ photocatalysts modified with various dyes. Compared with PtOX/KTa(Zr)O₃, dye-modified catalysts showed much larger water-splitting activity. Dye-modification effects were obtained with both water-soluble dyes (cyanocobalamin, rhodamine 6G, TPPS, rose bengal, TCPP, crystal violet, malachite green, fluorescein, and eosin Y) and water-insoluble dyes. In the case of water-soluble dyes, the dyes may adsorb on KTaO₃ and work as a promoter. While xathene based dyes including rhodamine 6G and rose bengal showed comparatively high positive effects on H₂ formation rate, fluorescein and eosin Y showed low modification effects. It is reported that H₂ production reached the plateau rapidly on Pt-TiO₂ sensitized with eosin or fluorescein dyes because of the easy photo-bleaching, [10]. In the case of triphenylmethane (crystal violet and malachite green), improvement in H₂ formation is smaller for malachite green than crystal violet. It is also reported that malachite green dissolves in water and degraded easier than that of crystal violet on dye sensitized SnO₂ [11]. The carotenoids involving capsanthin and β-carotene shows low activity to H₂ and O₂ formation. As for these molecules with long organic chain, the energy of excited singlet state tends to be consumed in molecular motion [12]. Thus, it seem to be difficult to convert a excited energy into photocatalytic water splitting reaction. In some photocatalysts, formation rates of H₂ were much higher than that of O₂. Photocatalytic water-decomposition on these catalysts is not stoichiometric to water, and the modifying dye might be decomposed as a sacrificial reagent. However, the improved photocatalytic activity cannot be simply explained by the effects of sacrificial effects of dyes because the amount of hydrogen molecules is much larger (few hundred times) than that of organic dye. Among the dyes examined, cyanocobalamin showed the highest activity. H₂ and O₂ formation rate were 1912 and 979 μmol g⁻¹ h⁻¹, respectively. Thus, dye modification is an effective method for improving the water-splitting activity of KTa(Zr)O₃ photocatalysts.

To understand the effects of an organic dye, the relationship between the redox properties of dyes and the H₂ formation rate was studied. Figure 3 shows the H₂ formation rate as a function of the reduction potential of dyes. It is evident that the H₂ formation rate depends strongly on the redox potential. A strong dependence is observed on

![Figure 3. Relationship between LUMO level of dye and H₂ formation rate. □: measure value, △: reference value from Ref. 13.](image-url)
the redox potential, and a high H₂ formation rate is obtained for a dye with a redox potential of -0.8 V vs. Ag/AgCl. This suggests that charge transfer from KTa(Zr)O₃ to the modification dye occurs, and an optimum redox potential exists for the modification dye to accept electrons from KTa(Zr)O₃. This assumption was further studied by a fluorescence spectroscopy.

UV-vis absorption spectra of KTaO₃ photocatalysts are shown in Figure 4a and b. The absorption edge of KTa(Zr)O₃ was observed around 355 nm, and the band gap of KTa(Zr)O₃ was estimated to be 3.5 eV, as mentioned above. A broad absorption peak, attributed to the Soret band absorption of Cr-TPP, was observed at 420 nm, as shown in Figure 4b. Q-band absorption peaks (500-700 nm) were also confirmed in the absorption spectrum of PtOX/Cr-TPP/KTa(Zr)O₃. Therefore, it was found that photoabsorption of the KTa(Zr)O₃ catalyst was expanded to the visible light region by dye modification. Figure 4c and d shows PL spectra of KTa(Zr)O₃ photocatalysts (excitation light: 266 nm). Maximum PL intensity was observed at 360 nm in both spectra, and the PL intensity of KTa(Zr)O₃ was decreased by Cr-TPP modification. This suggests that the excited energy was quenched by PL emission at 360 nm, and a Cr-TPP coating is effective for decreasing energy loss, which is resulted from an improved energy or charge transfer from KTa(Zr)O₃.

Figure 5 shows fluorescence spectra of Cr-TPP/KTa(Zr)O₃ with/without loading a PtOX co-catalyst, which is excited by visible light at 532 nm. And the excited electrons were quenched by PL emission at 665 nm. The PL intensity of Cr-TPP/KTa(Zr)O₃ was clearly decreased by loading PtOX. The relative PL intensity of the PtOX-loaded catalyst at 665 nm was 32.7%; thus, 67.3% of the excitation energy of Cr-TPP/KTa(Zr)O₃ may transfer to the PtOX promoter in this case. These results also suggest that the excitation energy of Cr-TPP transferred to the PtOX promoter. Therefore, the PL and UV-vis absorption spectra suggests that charge or energy transfer occurs from KTa(Zr)O₃ to Cr-TPP and further from Cr-TPP to PtOX promoter.

Figure 6 shows the fluorescence decay curves of KTa(Zr)O₃, Cr-TPP/KTa(Zr)O₃ and PtOX/Cr-TPP/KTa(Zr)O₃ at picoseconds levels. The fluorescence lifetime of KTa(Zr)O₃ decreased to an order of picoseconds by the surface modification with Cr-TPP. In case of an energy transfer process, both Förster-type (fluorescence resonance energy transfer) and Dexter-type (electron exchange energy transfer) are nonradiative processes. If an energy transfer occurred from KTa(Zr)O₃ to Cr-TPP, no influence on the fluorescence lifetime should be observed. Therefore, this result indicated that the electron transfer mainly occurred in the dye-modified KTa(Zr)O₃ photocatalyst at a few hundred picoseconds. Compared with dye modification, PtOX co-catalyst loading showed a negligible influence on the lifetime of the KTa(Zr)O₃ fluorescence. This result demonstrated that the excited charge in KTa(Zr)O₃ hardly transfer directly to the PtOX co-catalysts loaded on the Cr-TPP layers. The photo-generated electron in KTa(Zr)O₃ transferred to the Cr-TPP adsorbed on the KTa(Zr)O₃ surface. Our previous study shows that Cr-TPP/KTa(Zr)O₃ retained the excitation state for longer than 500 µs in contrast to that of KTa(Zr)O₃ returned to the normal state within 100 µs [6]. The fluorescence lifetime of metalloporphyrin is generally reported to be on the order of
nanoseconds [14, 15], and the phosphorescence yields of metallo-TPP complexes were extremely low (<0.0005), excepting for complexes that can observe an internal heavy atom effect (e.g., Pt- or Pd-TPP) [16]. Although the excitation of Cr-TPP might be occurred by energy transfer from KTa(Zr)O₃ in a dye-modified catalyst, it is not sufficient to explain the excitation state lasting several hundred microseconds. For this reason, a long-lived charge-separation state might be achieved by electron transfer from the excited state of KTa(Zr)O₃ to Cr-TPP in a dye-modified catalyst. Photocatalytic activity was improved by increasing the lifetime of photogenerated charges (e⁻ and h⁺) that can reach reaction sites on the surface of the catalyst. It was found that the excitation state of the KTa(Zr)O₃ photocatalyst can be improved by dye modification.

In order to confirm a two-step photo-excitation, the effects of wavelength on water splitting were further studied. Table 2 shows the wavelength dependence of the activity of KTa(Zr)O₃ photocatalysts. Although water splitting was achieved on dye-modified KTa(Zr)O₃ photocatalysts without wavelength filtering, the water-splitting reaction barely proceeded under Xe lamp irradiation with a UV cut-off filter (λ > 385 nm). In the case of a dye-sensitized TiO₂ photocatalyst, a photocatalytic reaction occurred with the injection of photoexcited electrons from the dye sensitizer to the conduction band of TiO₂ and H₂ formed with the concomitant oxidation of sacrificial reagents such as EDTA [17, 18]. Some porphyrins have appropriate energy potential for photocatalytic water splitting; however, a slow reaction rate of water oxidation with dye radical cations has been reported [19]. In photosynthesis of natural plants, the Mn cluster is adopted to catalyze the oxygen evolution reaction [20]. It seems that Cr-TPP radical cation was not sufficient to form oxygen from water. On the other hand, the formation rates of H₂ and O₂ on the dye-modified KTa(Zr)O₃ photocatalyst decreased considerably under irradiation only by UV light. This result obviously indicates that photoexcitation of the dye is important for achieving photocatalytic water splitting. However, a small amount of H₂ forms when only UV light is used. This suggests that energy transfer from KTa(Zr)O₃ to Cr-TPP is not large, and the excitation energy of KTa(Zr)O₃ seems to be quenched by charge transfer to Cr-TPP. Cr-TPP might be excited by charge transfer from KTa(Zr)O₃ in this system. In any case, excitation of both KTa(Zr)O₃ and the dye was necessary to achieve increased photocatalytic water-splitting activity on dye-modified KTa(Zr)O₃.

Estimated energy levels of KTa(Zr)O₃, Cr-TPP, and PtOₓ are shown in Figure 7 with H₂ and O₂ evolution potential. Here, the conduction and valence band energies of KTa(Zr)O₃ were adopted from references [9] and band gap estimated by UV-vis absorption spectrum. In the case of Cr-TPP, the HOMO and LUMO levels were determined from the redox potential and the band gap estimated by the photoabsorption/PL spectrum, respectively. As shown in Figure 7, the LUMO level of Cr-TPP was estimated to be about 0.4 V negative than the conduction band level of KTa(Zr)O₃. HOMO level of Cr-TPP is slightly negative than the oxygen evolution potential, water-splitting reaction cannot occur on Cr-TPP. Therefore, the estimated energy levels of the three component compounds satisfy the configuration of the Z-scheme model [1]. Considering the energy level shown in Figure 7, it is possible that photoexcited electrons in Cr-TPP first transferred to PtOₓ, and those in KTa(Zr)O₃ were transferred to the vacant band in the vacant LUMO level of Cr-TPP. PtOₓ co-catalyst and KTa(Zr)O₃ are possible formation sites for H₂ and O₂, respectively. This reaction scheme in two-step excitation is similar to the Tandem cell, which uses an oxide
semiconductor electrode and a dye-sensitized TiO$_2$ electrode for photolysis of water [21-24]. However, compared to the Tandem cell, a dye-modified KTa(Zr)O$_3$ photocatalyst has an architectural advantage, as it is a simple component that does not require an electrolyte such as an I$^{-}$/I$^{3-}$ redox pair. In PtO$_X$/Cr-TPP/KTa(Zr)O$_3$, charge separation was achieved by charge transfer between Cr-TPP and KTa(Zr)O$_3$, as mentioned above. Therefore, it was suggested that the photocatalytic activity of KTa(Zr)O$_3$ was improved by dye modification because of the suppression of recombination of photoexcited charge.

4. Conclusion

This study reveals that the water-splitting activity of KTa(Zr)O$_3$ photocatalyst was greatly improved by modification with various porphyrin dyes. Among the examined dye, modification with cyanocobalamin is the most effective for improving the activity and H$_2$ and O$_2$ formation rates were achieved as high as 1912 and 979 μmol g$_{cat}^{-1}$ h$^{-1}$, respectively. The formation rate of H$_2$ is almost double to that of O$_2$. Complete photocatalytic water splitting was achieved on this catalyst and it is also noted that the energy conversion efficiency was estimated to be about 0.013% in this photocatalyst under solar simulator (AM1.5). Cr-TPP dispersed on KTaO$_3$ surface improved the visible light absorption of KTaO$_3$ catalysts. The intensity of KTaO$_3$ photoluminescence (PL) was decreased by dye modification, and the PL intensity of the dye was also decreased by loading PtO$_X$ co-catalyst. This result suggested that the excitation energy was transferred between the components of dye-modified KTaO$_3$ photocatalysts. The excitation lifetime of KTaO$_3$ increased by dye modification, and an excitation state was sustained over few hundred microseconds [6]. Photoexcited electrons in KTaO$_3$ transferred to the dye, and a charge-separation state was achieved between KTaO$_3$ and the dye. This suggests that the photocatalytic activity was improved by increasing the lifetime of photoexcited charges that can reach the reaction sites effectively. The wavelength dependence of the activity of dye-modified KTaO$_3$ photocatalysts clearly indicated that the excitation of both KTaO$_3$ and the dye was essential for producing high amounts of H$_2$ and O$_2$. This suggests that two-step excitation occurred in dye-modified KTaO$_3$ photocatalysts. At present, it is assumed that PtO$_X$ works as H$_2$ and KTaO$_3$ as O$_2$ formation site, respectively. The lifetime of photoexcitation charge in KTaO$_3$ was prolonged by dye modification, and increased photocatalytic activity for water splitting was demonstrated. It was found that modification with porphyrin dye was effective for elevating the photocatalytic water-splitting activity. Consequently, dye modification is an effective method for improving the water-splitting activity of inorganic semiconductor photocatalysts.

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5. References
