

Dye-Modified Photocatalyst for Solar Water Splitting

Hidehisa Hagiwara

International Institute for Carbon-Neutral Energy Research (I²CNER), Hydrogen Production Division

Photocatalytic water splitting is one of the most ideal and effective solution for the current global energy and environmental issues. In the photocatalytic reaction process, photogenerated electrons and holes in a semiconductor photocatalyst migrate to the surface, and redox reactions take place on active sites such as cocatalysts. A prolonged excited state of the photocatalyst is important for achieving high photocatalytic activity. In our previous research, the photocatalytic activity of Zr-doped KTaO₃ (KTa(Zr)O₃) was improved by modification with porphyrin dyes.^[1] In this study, the mechanism for the positive effects of porphyrin modification on the H₂ formation rate was studied.

Table 1 shows the wavelength dependence of the activity of KTa(Zr)O₃ photocatalysts. Although water splitting was achieved on dye-modified KTaO₃ photocatalysts without wavelength filtering, the water-splitting reaction negligibly proceeded under Xe lamp irradiation with a UV cut-off condition ($\lambda > 385$ nm). The formation rates of H₂ and O₂ on the dye-modified KTaO₃ photocatalyst decreased considerably under irradiation only by UV light ($\lambda < 380$ nm). This result obviously indicates that photoexcitation of the dye is important for achieving photocatalytic water splitting. In this catalyst, excitation of both KTaO₃ and the dye was necessary to achieve the improved photocatalytic water-splitting activity. Fig. 1 shows the decay curves of the observed photovoltaic potential of catalysts after irradiation with a fourth-harmonic beam (266 nm) of a Nd-YAG laser for 5 ns. Compared with the results of KTa(Zr)O₃, the half-life of Cr-TPP/CTa(Zr)O₃ is almost one order of magnitude longer. Therefore, the positive effects of the dye modification are brought about by the improvement of KTa(Zr)O₃ excitation lifetime. The excited charge in dye-modified KTa(Zr)O₃ can reach to the reaction sites more smoothly and effectively. As shown in Fig. 2, the reaction scheme of dye-modified KTa(Zr)O₃ photocatalyst is two-step excitation similar with photosynthesis. Unlike dye-sensitized solar cell, excited electron in dyes mainly transfers directly to contacted Pt co-catalyst which is active site for H₂ formation. Excited electron in KTa(Zr)O₃ would be consumed by reduction of dye modified, and water oxidation reaction occurred on KTa(Zr)O₃ surface.

This study reveals the charge transfer mechanism of dye-modified KTa(Zr)O₃ photocatalyst for water splitting. Modification with porphyrin dye was found to be effective for elevating the photocatalytic water-splitting activity. Consequently, dye modification has the potential to be an effective method for improving the water-splitting activity of inorganic semiconductor photocatalysts.

Table 1. Wavelength dependence of the activity of KTa(Zr)O₃ photocatalysts.^a

| Catalyst | Light | Formation rate / $\mu\text{mol g}_{\text{cat}}^{-1}\text{h}^{-1}$ | |
|---|--------------------------|---|----------------|
| | | H ₂ | O ₂ |
| PtO _x /Cr-TPP /KTa(Zr)O ₃ | Full arc | 513 | 257 |
| | $\lambda > 385$ nm | 0.24 | Trace |
| | UV ($\lambda < 380$ nm) | 51.4 | 23.2 |
| PtO _x /KTa(Zr)O ₃ | Full arc | 2.1 | 0.7 |

^aLight source: 500 W Xe lamp; Amount of dye: 1.2 μmol ; pH: 11.

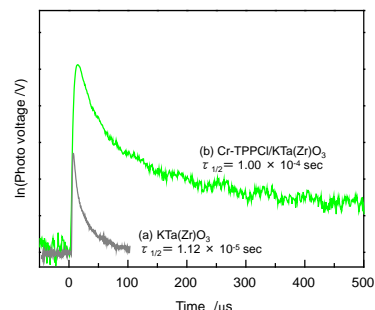


Fig. 1 Decay curve of the photovoltaic potential of KTa(Zr)O₃ modified by (a) none and (b) Cr-TPP/CTa(Zr)O₃ (Ex: 266 nm Nd-YAG laser).

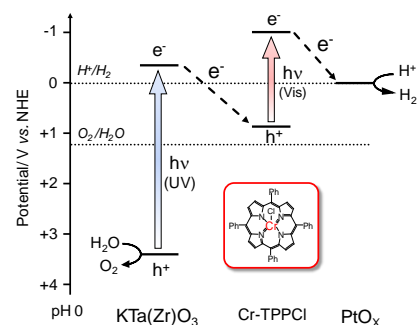


Fig.2 Charge transfer mechanism in dye-modified KTa(Zr)O₃ photocatalyst.

[1] H. Hagiwara, et al., *Angew. Chem Int. Ed.* 45 (2006) 1420.