

## Dye-Modified Photocatalyst for Solar Water Splitting

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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 KTaO<sub>3</sub> (KTa(Zr)O<sub>3</sub>) was improved by modification with porphyrin dyes.<sup>[1]</sup> In this study, the mechanism for the positive effects of porphyrin modification on the H<sub>2</sub> formation rate was studied.

Table 1 shows the wavelength dependence of the activity of KTa(Zr)O<sub>3</sub> photocatalysts. Although water splitting was achieved on dye-modified KTaO<sub>3</sub> 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 H<sub>2</sub> and O<sub>2</sub> on the dye-modified KTaO<sub>3</sub> 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 KTaO<sub>3</sub> 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)O<sub>3</sub>, the half-life of Cr-TPP/CTa(Zr)O<sub>3</sub> is almost one order of magnitude longer. Therefore, the positive effects of the dye modification are brought about by the improvement of KTa(Zr)O<sub>3</sub> excitation lifetime. The excited charge in dye-modified KTa(Zr)O<sub>3</sub> can reach to the reaction sites more smoothly and effectively. As shown in Fig. 2, the reaction scheme of dye-modified KTa(Zr)O<sub>3</sub> 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 H<sub>2</sub> formation. Excited electron in KTa(Zr)O<sub>3</sub> would be consumed by reduction of dye modified, and water oxidation reaction occurred on KTa(Zr)O<sub>3</sub> surface.

This study reveals the charge transfer mechanism of dye-modified KTa(Zr)O<sub>3</sub> 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)O<sub>3</sub> photocatalysts.<sup>a</sup>

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

<sup>a</sup>Light source: 500 W Xe lamp; Amount of dye: 1.2  $\mu\text{mol}$ ; pH: 11.

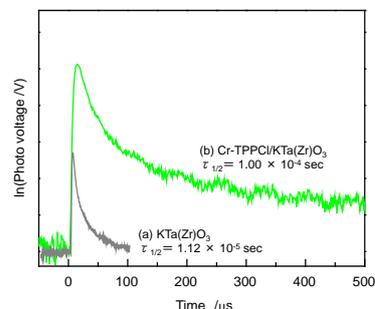


Fig. 1 Decay curve of the photovoltaic potential of KTa(Zr)O<sub>3</sub> modified by (a) none and (b) Cr-TPP/CTa(Zr)O<sub>3</sub> (Ex: 266 nm Nd-YAG laser).

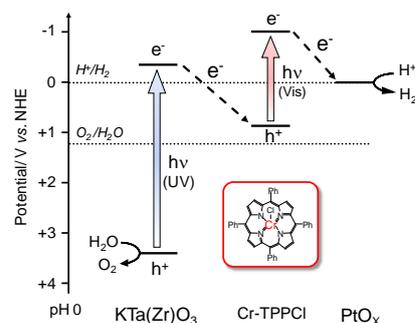


Fig.2 Charge transfer mechanism in dye-modified KTa(Zr)O<sub>3</sub> photocatalyst.

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