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Research paper

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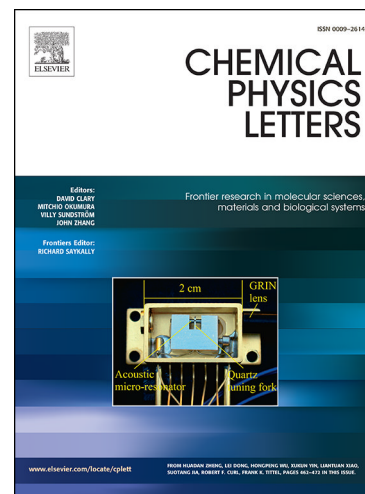
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# Correlation between surface carrier dynamics and water oxidation activity of commercially available rutile-type TiO<sub>2</sub> powders

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## Abstract

We studied the correlation between carrier characters and water oxidation activity of commercially available rutile-type TiO<sub>2</sub> powders by global and target analysis of time-resolved transient diffuse reflection spectra. The whole observed data-set were well fitted by the target analysis using three independent components. Spectral shape of surface carriers and their time evolution obtained by the target analysis have intimate relation in the water-oxidation activities. A series of this type of investigation will contribute to the breakthrough of the material design for promising photocatalyst.

*Keywords:* Photocatalytic water oxidation; Carrier dynamics; Global and target analysis; Transient absorption; Titanium dioxide

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## 1. Introduction

Semiconductor photocatalysts are known as key materials that can utilize solar energy as a source to realize artificial photosynthesis [1-3]. In order to enhance the quantum yield of photocatalytic reaction, elucidation of the factors that determine the activity of photocatalyst has been extensively investigated [4-6]. Because the redox reaction of a semiconductor occurs through transferring carriers generated by photoirradiation, characterization of the carriers is the issue of importance to be correctly addressed for the purpose to investigate photocatalytic reactions. A number of studies have already been conducted to determine the carrier characteristics using photoluminescence [7-9], time-resolved [10-16], and photoacoustic [17-21] analyses. Time-resolved transient absorption spectroscopy is one of the most valuable tools that can determine the behaviours of carrier dynamics from femtosecond to millisecond time regime.

For example, in anatase TiO<sub>2</sub>, it is reported that the surface trapped electrons give rise to the transient absorption signal at 800 nm, free electrons in the infrared spectral region, and surface trap holes at 500 nm [14]. Yamakata et al. reported that the water splitting activity of NaTaO<sub>3</sub> based catalysts increases with the increase of the lifetime of the free electrons [13]. Matsumoto et al. investigated the relationship between the particle size of BiVO<sub>4</sub> and carrier lifetimes. They claimed that the particle size of the catalyst affects the photooxidation activity [16]. On the other hand, the absorption energies of surface carriers of a photocatalyst depend on the surface structure because the trap levels of the photocatalyst vary depending on the species of surface defects. Ohtani et al. evaluated distribution of trap energy levels using reversed double-beam photoacoustic spectroscopy [20, 21].

However, studies have not yet been conducted so far to reveal a correlation between the properties and the quantum

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