

# Difference in the Behavior of Photogenerated Electrons and Holes on Anatase and Rutile TiO<sub>2</sub> Powders

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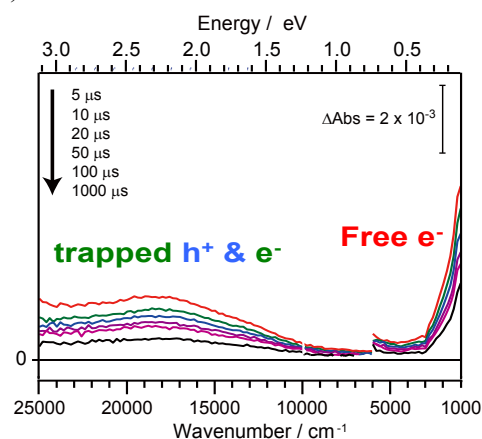
TiO<sub>2</sub> is one of the most often used material as photocatalysts. In many reactions, anatase TiO<sub>2</sub> exhibits higher activity than rutile TiO<sub>2</sub>, but rutile TiO<sub>2</sub> exhibits higher activity for water oxidation. However, the mechanism responsible for the difference in their photocatalytic activity had been a longstanding question for more than 40 years. In this work, the mechanism that determines the difference in photocatalytic activities between anatase and rutile TiO<sub>2</sub> powders have been studied by femtosecond to millisecond time-resolved visible to mid-IR absorption spectroscopy [1-3].

Figure 1 shows time-resolved absorption spectra of anatase TiO<sub>2</sub> powders upon bandgap excitation. In the case of anatase TiO<sub>2</sub> powder, strong absorption was observed at 4000-1000 cm<sup>-1</sup>, which is assigned to intraband transition of free electrons in the conduction band (CB) and/or excitation of shallowly trapped electrons to CB. We found that a considerable number of free electrons are surviving for longer than 1 ms. On the contrary, in the case of rutile TiO<sub>2</sub> powder, the free electrons are absent in microsecond domain (Fig. 2): the free electrons are rapidly trapped at defects within a few picosecond and only a trace amount of free electrons can survive for 1 ms. In rutile TiO<sub>2</sub>, a broad peak was observed at 17000-7000 cm<sup>-1</sup>, which was assigned to the optical transition of deeply trapped electrons from the mid-gap state to CB. The depth was estimated to be >0.9 eV from the absorption edge (7000 cm<sup>-1</sup>, ~0.9 eV), which is much deeper than that in anatase TiO<sub>2</sub> (<1000 cm<sup>-1</sup>, < 0.1 eV). The difference in the electron trap depth and the lifetime of free or shallowly trapped electrons is responsible for the higher activity of anatase TiO<sub>2</sub> for reduction reactions. However, the deep electron trapping in rutile TiO<sub>2</sub> positively acts to prevent recombination;

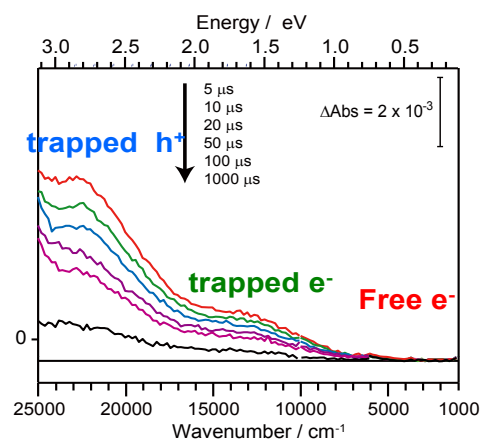
thereby extending the lifetimes of both holes and deeply trapped electrons. As a result, the number of holes surviving in rutile TiO<sub>2</sub>, giving a strong absorption at 25000~17000 cm<sup>-1</sup>, becomes much larger than in anatase TiO<sub>2</sub> (Figs. 1 & 2). The longer lifetime of holes promotes photocatalytic oxidation, especially for multi-hole processes such as water oxidation. These findings strongly suggest that the defects in TiO<sub>2</sub> powder particles induce peculiar behaviors of charge carriers, which determine the distinctive photocatalytic activities of anatase and rutile TiO<sub>2</sub> powders. In addition, we note that these behaviors of photogenerated charge carriers in powder particles are totally different from that in defect-free single crystals [2].

## REFERENCES

- [1] A. Yamakata et al.: *J. Phys. Chem. C*, **118** (2014) 23897-23906.
- [2] A. Yamakata et al.: *J. Phys. Chem. C*, **119** (2015) 1880-1885.
- [3] A. Yamakata et al.: *J. Phys. Chem. C*, **119** (2015) 24538-24545.



**Figure 1.** Transient absorption spectra of anatase TiO<sub>2</sub> powder (TIO-10) irradiated by UV laser pulses (355 nm, 6-ns duration, 0.5 mJ per pulse, and 5 Hz).



**Figure 2.** Transient absorption spectra of rutile TiO<sub>2</sub> powder (TIO-6) irradiated by UV laser pulses (355 nm, 6-ns duration, 0.5 mJ per pulse, and 5 Hz).