Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2018

Supplementary Information

Structural Changes of Water Molecules during Photoelectrochemical Water Oxidation on TiO_2 Thin Film Electrodes

Chandana Sampath Kumara Ranasinghe[a] *and Akira Yamakata*[a,b*]

[a] Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan

[b] Cooperative Research Fellow, Institute for Catalysis, Hokkaido University, Hokkaido 001-0021, Japan

1. XRD patterns of FTO/TiO_2 thin film used in this experiment.

FTO/TiO_2 thin film was fabricated on the sapphire prism as described in section 2.1. To confirm the structure of the TiO_2 deposited by this technique, a similar thin film was fabricated on flat glass substrate by following the same experimental methods for XRD measurements. The XRD patterns were measured by using Rigaku, Ultima IV X-ray diffractometer (Cu Kα radiation, λ = 0.154 nm). The XRD pattern of the thin film is shown in Fig. S1. The formation of anatase TiO_2 (JCPDS card no. 21-1272) was confirmed by the clear peaks of (101), (200), and (211).[1]

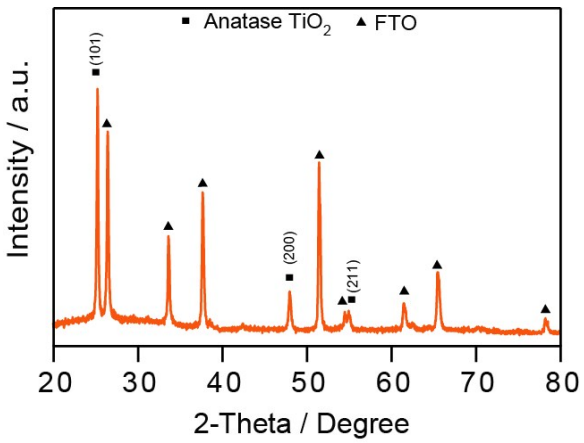

Fig. S1. XRD pattern of the FTO/TiO_2 thin film used in this work.

2. Scanning electron microscopic images of FTO/TiO_2 thin film.

FTO/TiO_2 thin film was fabricated on the sapphire prism. For the SEM measurements, we fabricated the TiO_2 thin film on FTO flat glass substrate (Thickness-2 mm, Area- 2 cm x 2 cm). SEM images of the TiO_2 thin film are shown in Fig. S2 (A~C). The cross-sectional image of the TiO_2 layer is also shown in Fig. S2 (D). The average thickness of the TiO_2 layer was estimated to be ~750 nm. These results are well agreed with our previous reports.[2, 3]

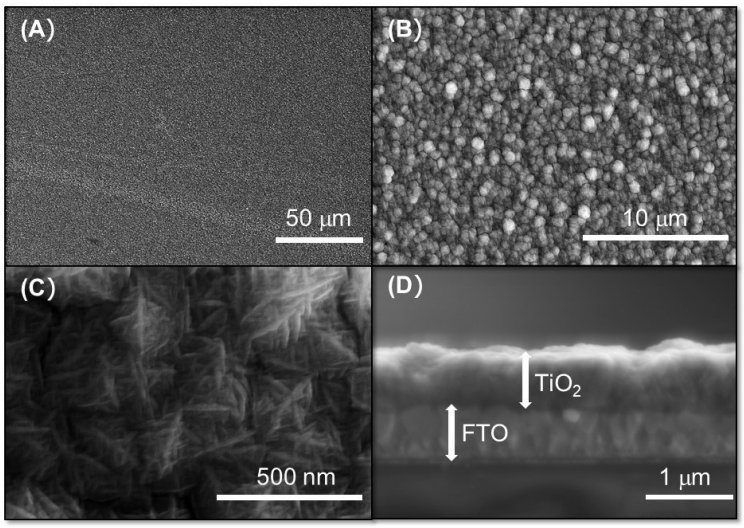

Fig. S2. Scanning electron microscopy (SEM) images of the surface morphology of FTO/TiO_2 thin film (A~C) and the cross section image (D).

3. UV-Vis transmission spectra of TiO_2 thin film used in this work and that fabricated from anatase TiO_2 powder.

We have compared the UV-Vis absorption spectra of the TiO_2 thin films used in this work and that fabricated by spray pyrolysis deposition (SPD) from anatase TiO_2 powder (TIO-1, Catalyst Society of Japan: particle size 21 nm).[2].

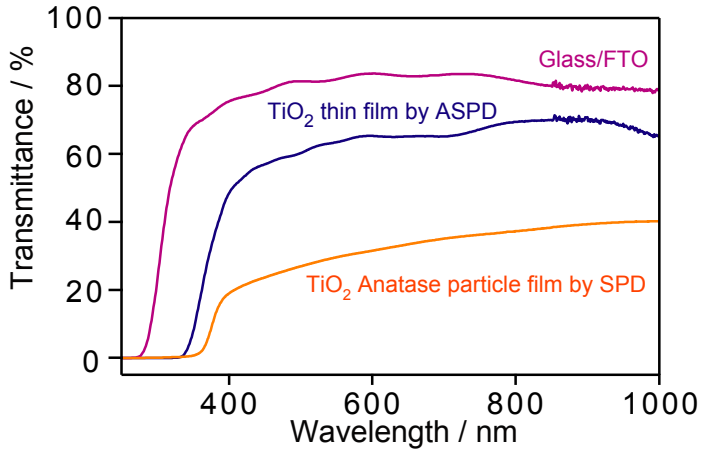

Fig. S3. Transmission spectra of FTO layer, TiO_2 thin films, and TiO_2 anatase powder based electrodes fabricated on glass substrate.

4. Irradiated UV-power dependence of photocurrent.

Photocurrent of TiO_2 thin film electrode was measured under different powers of UV light (Fig. S4 (A)). The photocurrent density recorded at 1.0 V was plotted vs. UV power density (Fig. S4 (B)). The photocurrent density was linearly increased with the irradiated UV power.

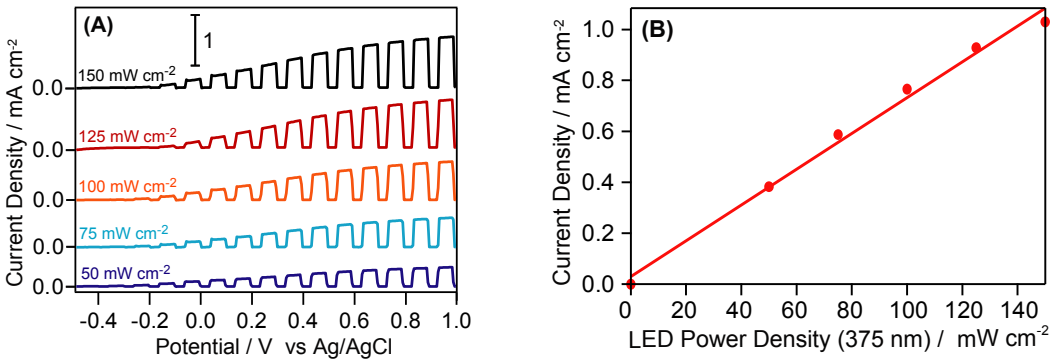

Fig. S4. (A) Photocurrent response of the TiO_2 thin film under different power densities of LED light (375 nm, 0.1 Hz) measured in 0.1 M Na_2SO_4 aqueous solution (H_2O) at positive potential sweep -0.5 to 1.0 V and (B) Plot of photocurrent density at 1.0 V vs. different illumination power densities of LED light.

5. Laser power dependence of the decay kinetics of photogenerated electrons.

We fabricate the same TiO_2 thin film on a CaF_2 plate, and the laser power dependence of the lifetime of photogenerated charge carriers was investigated in a vacuum. According to Fig. S5 (A), the absolute intensity of the transient absorption at 2500 cm^{-1} gradually increased with increasing the laser power, but these decay curves are almost parallel after 2 μs. Fig. S5 (B) shows that the absorption intensity at 2 μs. The non-linear dependence to the laser power is due to the 2nd-order recombination kinetics of photogenerated charge carriers proceeding within 2 μs.

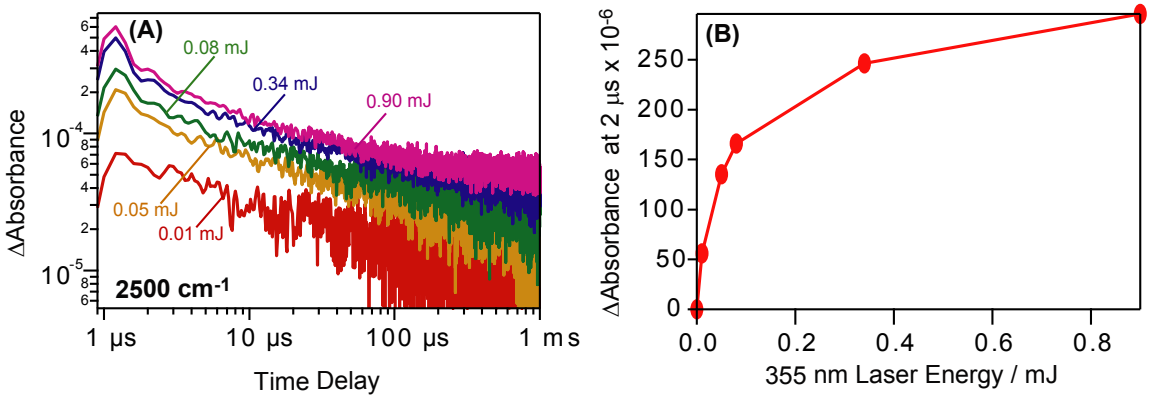

Fig. S5. (A) Decay curves of photogenerated electrons (2500 cm^{-1}) in the TiO_2 thin film measured in a vacuum. The film was photoexcited by 355 nm laser pulses with different power (repetition rate: 0.05 Hz). (B) The intensity of transient absorption measured at 2 μs vs. power of the laser (355 nm).

6. Stability of the photocurrent of TiO_2 thin film fused in this work.

The stability of the TiO_2 thin film under UV light irradiation (375 nm, 0.1 Hz) was examined (Fig. S6). The photocurrent did not degrade even after 1000 s, suggesting this TIO_2 electrode is very stable as reported in our previous studies.[2]

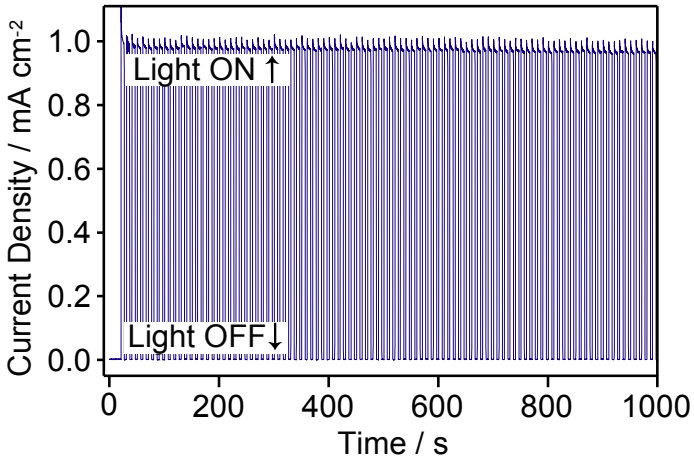

Fig. S6. Photocurrent response (at 1.0 V) of the TiO_2 thin film under illumination of LED light (375 nm, 0.1 Hz) measured in 0.1 M Na_2SO_4 aqueous solution (H_2O) with the time.

7. Effects of laser pulse irradiation on FTO layer.

Transient absorption spectra of fluorine doped tin oxide (FTO) after UV laser pulse irradiation was measured as shown in Fig. S7. However, no signal was observed. Therefore, the effects of photoirradiation of FTO can be neglected.

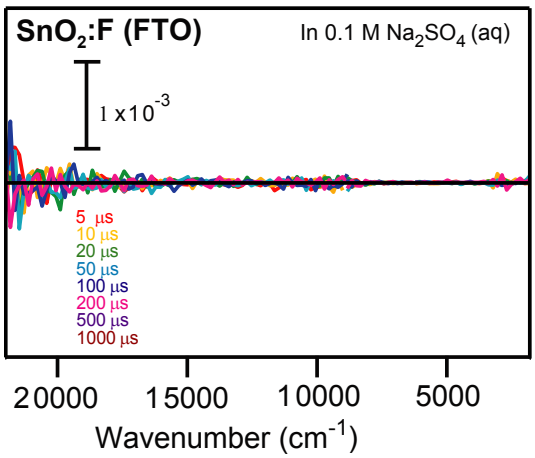

Fig. S7. Transient absorption spectra of FTO thin film in 0.1 M Na_2SO_4 (aq) measured without applying a bias potential. Spectra were recorded at 5-1000 μs after irradiation by 355 nm laser pulses (0.2 mJ $pulse^{-1}$ with the repetition rate of 5 Hz).

8. Expansion of Figures 3 and 4 for the detailed comparison with Figure 7.

In order to compare Fig. 3 and 4 with Fig. 7, the x-axis of Fig. 3 and 4 were expanded and re-plotted as Fig. S8 and S9, respectively. However, the spectral shape is almost identical: the new positive peak appeared at 3600 cm^{-1}, and negative peak appeared at ~3200 cm^{-1}.

sa

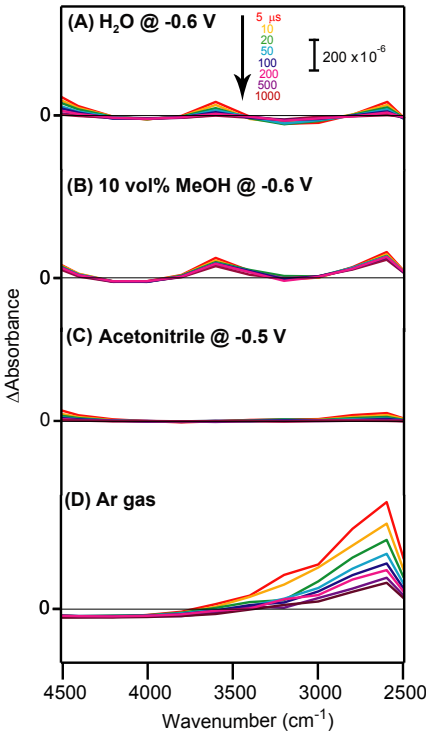

Fig. S8. Expansion of x-axis of Figure 3 (4500 - 2500 cm^{-1}). See Figure caption of Fig. 3.

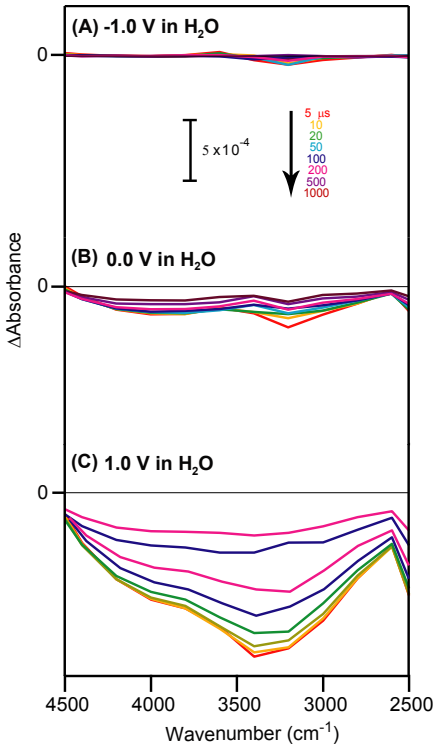

Fig. S9. Expansion of x-axis of Figure 4 (4500 - 2500 cm^{-1}). See Figure caption of Fig. 4.

References

1. J. Yu and J. Zhang, *Dalton Trans*, 2010, **39**, 5860-5867.
2. C. S. K. Ranasinghe, J. J. M. Vequizo and A. Yamakata, *J. Photochem. Photobiol. A: Chem.*, 2017, DOI: https://doi.org/10.1016/j.jphotochem.2017.09.006.
3. G. R. A. Kumara, C. S. K. Ranasinghe, E. N. Jayaweera, H. M. N. Bandara, M. Okuya and R. M. G. Rajapakse, *J. Phys. Chem. C*, 2014, **118**, 16479-16485.