Mid-infrared absorption of trapped electrons in titanium(IV) oxide particles using a photoacoustic FTIR technique

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Materials

The analytical grade reagents ethanol, deuterium oxide (D_2O) and other chemicals were used without further purification. ST-01 and ST-41 (Ishihara Sangyo Co.) and AMT-600 (TAYCA Co.) as commercial anatase TiO_2 powders, MT-150A, MT-600B (TAYCA Co.) and CR-EL (Ishihara Sangyo Co.) as commercial rutile TiO_2 powders, and commercial brookite TiO_2 powders (Kojundo Chemical Laboratory Co.) were used.

FTIR-PAS measurements

Detailed setups for FTIR-PAS measurements were reported previously.[1] A home-made PA cell composed of a duralumin body with an inner volume of ca. 0.2 mL (8 mmΦ x 4 mmH), a calcium fluoride (CaF_2) window and two valves for gas exchange was used. An FTIR spectrometer (Nicolet, iS10) was used as interference IR sources, and mirror velocity was 0.3165 cm s^{-1}. The digital PA signal acquired by a digital MEMS microphone (TDK InvenSense, ICS-43432) buried in the cell was recorded by using a PC equipped with digital I/O devices. The interferrogram acquired by analogue conversion of the digital PA signal was Fourier-transformed with the Happ-Genzel window function, and the PA spectra were obtained by normalizing with carbon black powder (Kojundo Chemical Laboratory Co.) as a reference to compensate wavenumber-dependent light intensity. Fig. S1 shows a non-normalized PA spectrum of carbon black powder. PA intensity is sufficiently high for measurements in the wavenumber region of 900–6000 cm^{-1}. A TiO_2 sample was placed in the PA cell, and nitrogen with ethanol vapour was flowed into the PA cell. Then flow of only nitrogen was carried out in order to remove the unnecessary amount of ethanol. FTIR measurements were carried out after shutting off the valves, i.e., in a closed system at room temperature. Ultraviolet

(UV) irradiation was performed through a window on the top of the cell using a light-emitting diode (Nichia NCSU033B, emitting around 365 nm, 8.8 mW cm^{-2}).

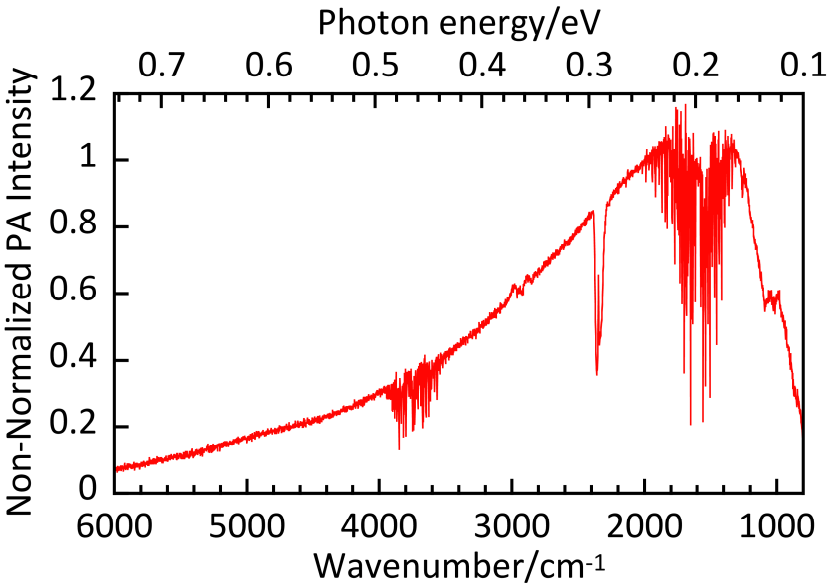

Fig. S1 Non-normalized PA spectrum of carbon black powder.

Table 1 Physical and Chemical Properties of Samples. [a] Reported in ref 3. [b] Reported in ref 4. [c] Reported in ref 5. [d] Reported in ref 2.

Name	supplier	crystal structure	Specific surface area / $m^2\ g^{-1}$	Ti^{3+} density /μmol g^{-1}
ST-01	Ishihara Sangyo	anatase	344[a]	118[d]
AMT-600	TAYCA	anatase	55[a]	72[d]
ST-41	Ishihara Sangyo	anatase	11[a]	32
MT-150A	TAYCA	rutile	114[a]	125
MT-600B	TAYCA	rutile	27[b]	71
CR-EL	Ishihara Sangyo	rutile	8[a]	21[d]
Brookite	Kojundo Chemical Laboratory	brookite	23[c]	40

Measurements of Ti^{3+} density

The Ti^{3+} density in a TiO_2 sample was measured by the time course of PAS in UV-visible region. The detailed procedure for the measurements was reported previously.[2] PAS analysis was carried out using a gas-exchange PA cell. The atmosphere in the cell was controlled by a flow of nitrogen containing ethanol vapor, and measurements were conducted in a closed system at room temperature. A light-emitting diode (LED) emitting at ca. 625 nm (Luxeon LXHL-ND98) was used as the probe light, and the output intensity was modulated by a digital function generator (NF DF1905) at 80 Hz. In addition to the modulated light, a UV-LED (Nichia NCCU033B, emitting at ca. 365 nm, 2.5 mW cm^{-2}) was used. The PAS signal acquired by a condenser microphone inserted in the cell was amplified and monitored by a digital lock-in amplifier (NF LI5640). From the saturated PA intensity of each sample, Ti^{3+} density was estimated.

Repeated experiment

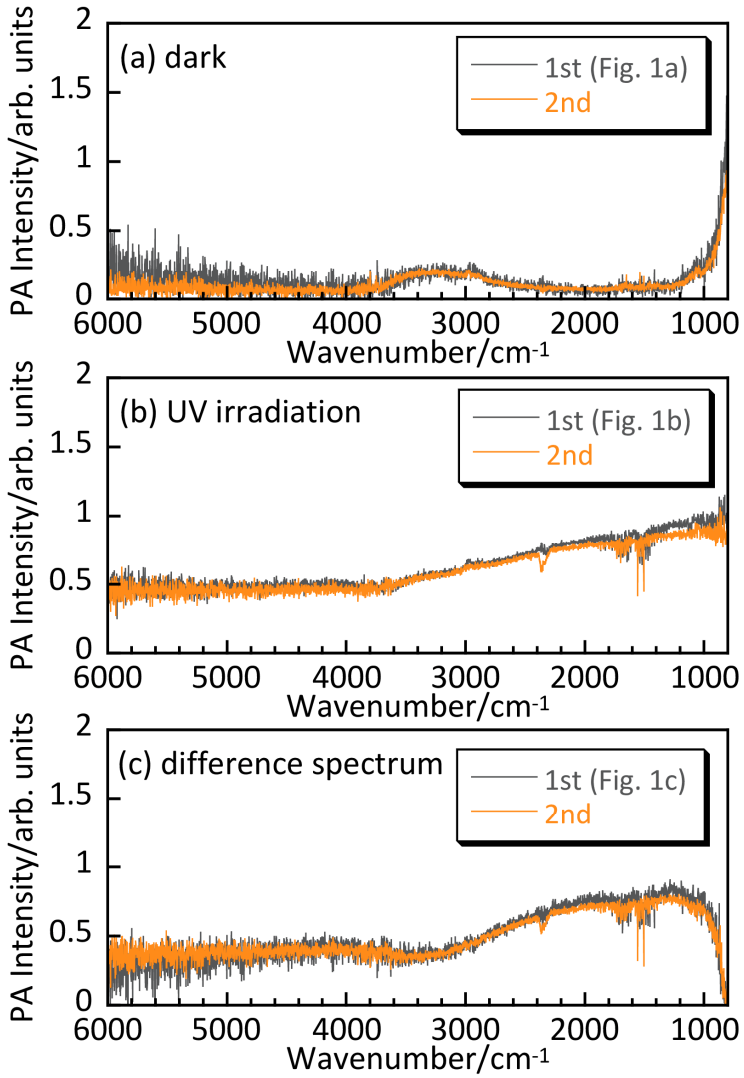

Fig. S2 FTIR-PAS spectra of anatase TiO_2 (AM-T600) with adsorbed ethanol under nitrogen (a) before and (b) after UV irradiation and (c) difference spectrum between (a) and (b).

FTIR-PAS spectra of anatase TiO_2

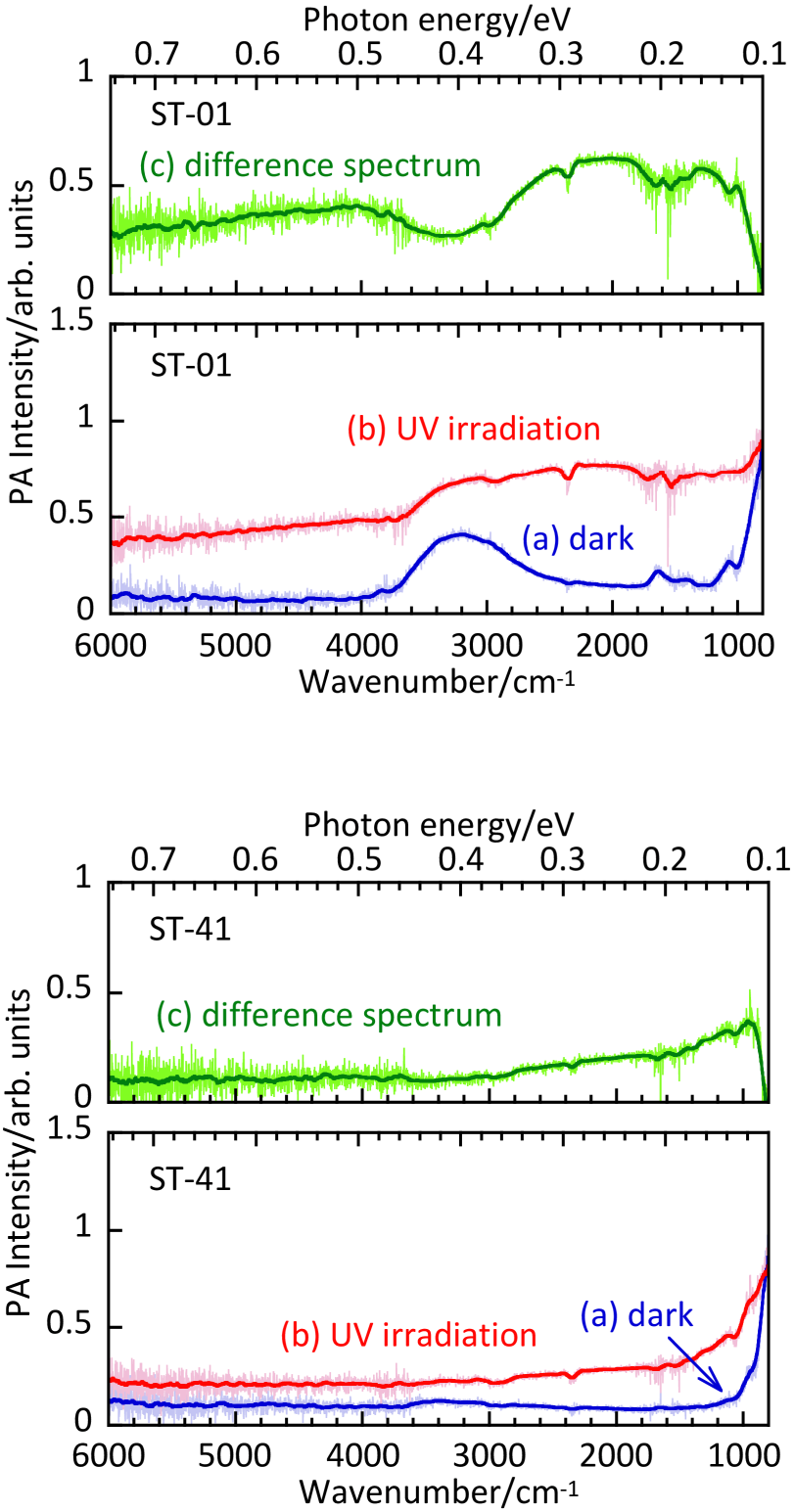

Fig. S3 FTIR-PAS spectra of anatase TiO_2 (ST-01, ST-41) with adsorbed ethanol under nitrogen (a) before and (b) after UV irradiation and (c) difference spectrum between (a) and (b). Blue, red and green lines are smoothed spectra by 33 point moving average of original data (pale blue, pink and yellow green lines).

FTIR-PAS spectra of rutile TiO_2

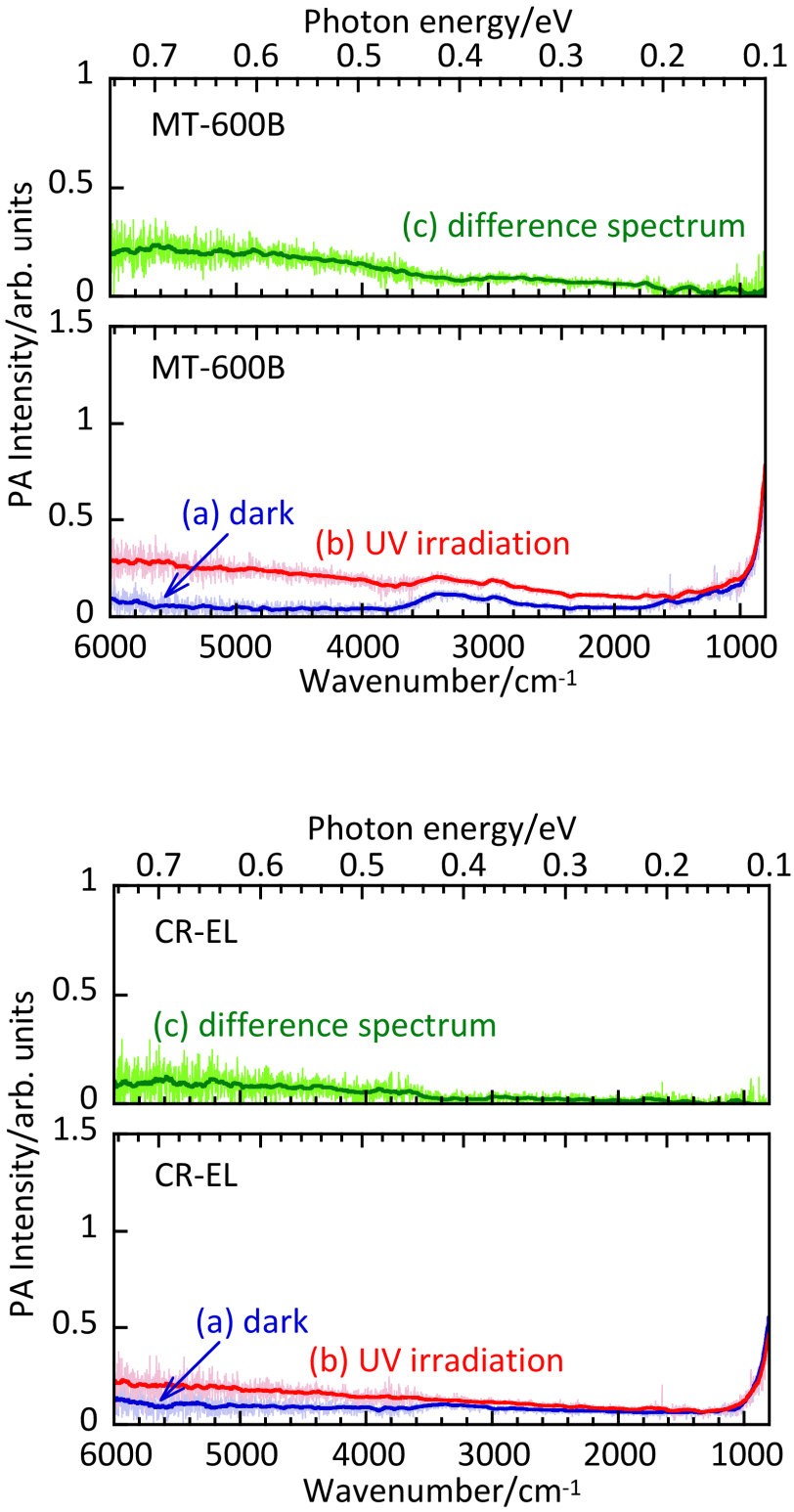

Fig. S4 FTIR-PAS spectra of rutile TiO_2 (MT-600, CR-EL) with adsorbed ethanol under nitrogen (a) before and (b) after UV irradiation and (c) difference spectrum between (a) and (b). Blue, red and green lines are smoothed spectra by 33 point moving average of original data (pale blue, pink and yellow green lines).

References

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