

## Electronic supplementary information

### ***In situ* photoacoustic analysis of near-infrared absorption of rhodium-doped strontium titanate photocatalyst powder**

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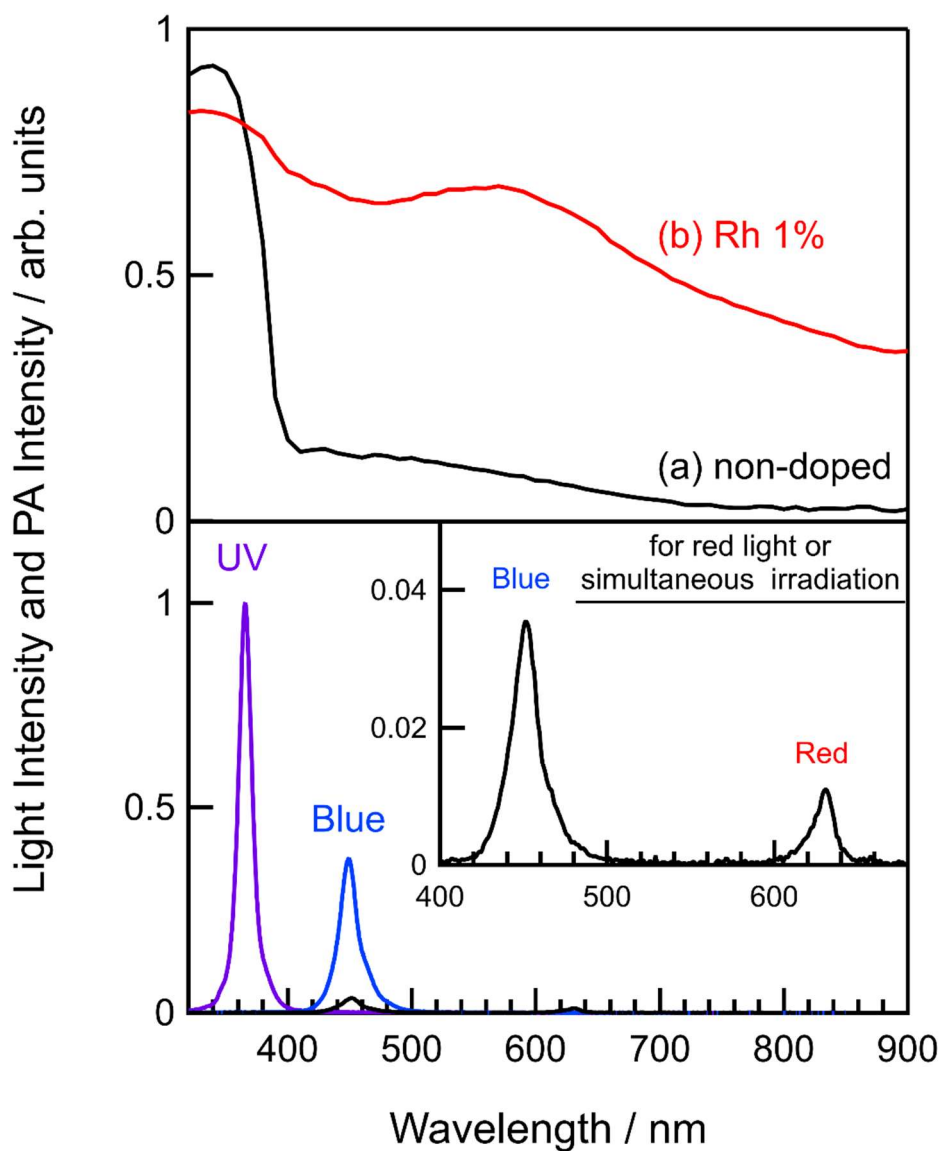
**UVVISNIR-PAS measurements** Two types of PA cells, a sealed-type cell and an atmosphere control-type cell equipped with two gas-exchange valves, were used. These cells were composed of a duralumin body, a quartz window and a digital MEMS microphone (STMicroelectronics Inc., STEVAL-MKI155V2). About 20 mg of a powder sample was placed in a sample holder and then loaded on the PA cell. Monochromatic light was extracted from a 300 W xenon lamp (Cemax, LX-300F) and halogen lamp (Asahi Spectra, FHL-101) using a grating monochromator (JASCO, CT-10T), and its intensity was modulated by an optical shutter at 12.8 Hz. Measurements were carried out in a closed system at room temperature and 1 atm pressure using light in the wavelength range of 320-900 nm in 10-nm or 5-nm steps. The PA signal due to photoabsorption of a sample was acquired by a digital MEMS microphone and Fourier-transformed with a Hamming window function. The UVVISNIR-PAS spectra were obtained by normalizing with carbon black powder (Kojundo Chemical Laboratory Co.) as a reference. In the measurement using an atmosphere control-type cell, the atmosphere in the PA cell was controlled by a flow of nitrogen (N<sub>2</sub>) gas with ethanol vapour. An excess amount of ethanol vapour in the cell was removed by flowing only N<sub>2</sub> gas because detection of absorption of a sample in the atmosphere control-type cell is disturbed by ethanol in a gas phase. Ethanol under the condition is denoted as adsorbed ethanol. The sample was irradiated with UV light from the same side as that of the probe light using a light-emitting diode (LED) (Nichia, NCSU033B, emission around 365 nm, 8.0 mW cm<sup>-2</sup>).

**FTIR-PAS measurements** The FTIR-PAS system has been described in detail in previous reports.<sup>1,2</sup> The PA cell composed of a duralumin body, a calcium fluoride (CaF<sub>2</sub>) window,

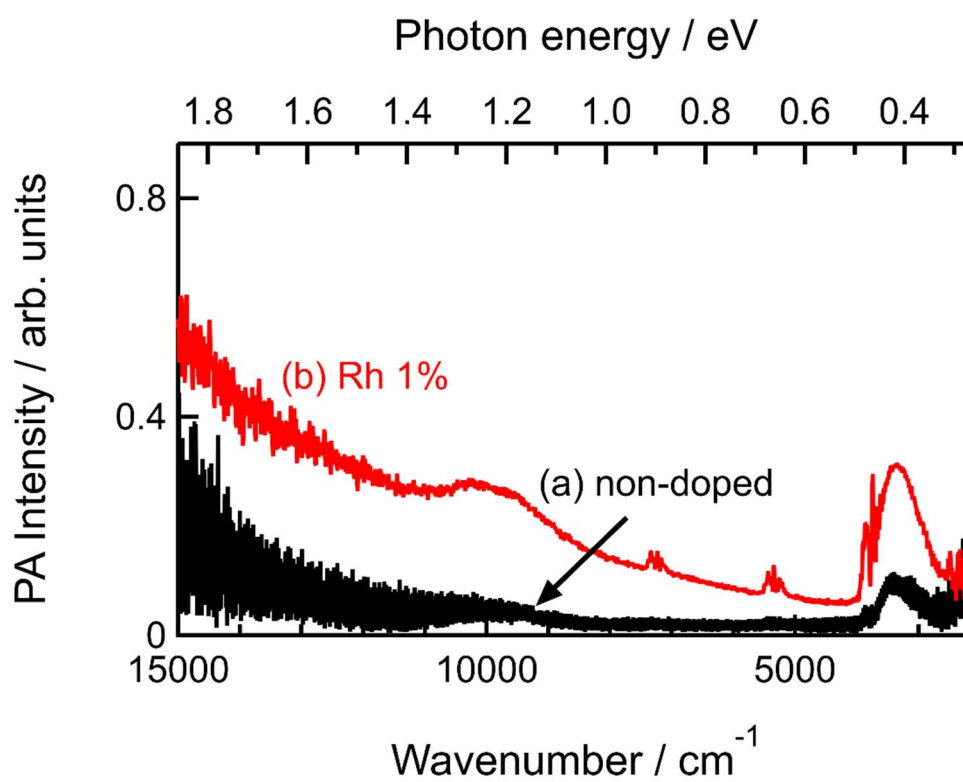
two gas-exchange valves for atmosphere control and a digital MEMS microphone (TDK InvenSense, ICS-43432) was used. An FT-NIR spectrometer (PerkinElmer, Frontier NIR, mirror velocity:  $0.1 \text{ cm s}^{-1}$ ) was used as a probe source.  $\text{N}_2$  or oxygen ( $\text{O}_2$ ) gas containing ethanol vapour was used for controlling the atmosphere in the PA cell. The atmosphere is denoted as ethanol-saturated  $\text{N}_2$  or  $\text{O}_2$ . In the case of analysis of the change in a steady state under light irradiation for a long time, an excess amount of ethanol in the cell was removed by flowing only  $\text{N}_2$  gas. Ethanol under the condition is denoted as adsorbed ethanol. About 20-100 mg of a powder sample was placed in a sample holder consisting of a duralumin body (with an inner volume of *ca.* 0.03 or 0.08 mL) and a  $\text{CaF}_2$  window and then loaded on the PA cell. The sample was irradiated with excited light from the same side as that of the probe light using LEDs emitting around 365, 455 and 625 nm (Nichia, NCSU033B; New Energy, XPGDRY-L1-0000-00601-SB01; OSRAM SYLVANIA, LZ4-VOMDOC-0000) (Fig. S1), and these intensities were 8.8, 8.4 and  $8.4 \text{ mW cm}^{-2}$ , respectively. Measurements were carried out in a closed system at room temperature and 1 atm pressure in the wavenumber range of  $15000\text{-}2100 \text{ cm}^{-1}$ . The PA signal was acquired by a digital MEMS microphone and Fourier-transformed with a Hap-Genzel window function. The FTIR-PAS spectra were obtained by normalizing with carbon black powder as a reference.

### Supplementary References

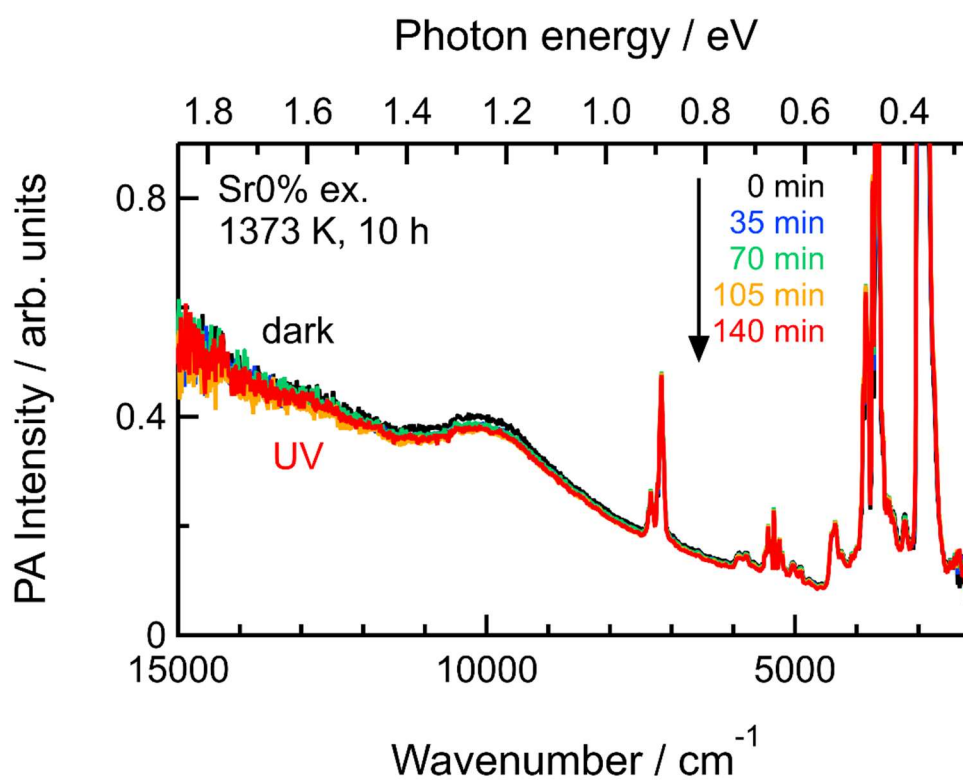
- (1) N. Murakami and N. Koga, *Catal. Commun.*, 2016, **83**, 1–4.
- (2) T. Shinoda and N. Murakami, *J. Phys. Chem. C*, 2019, **123**, 12169–12175.



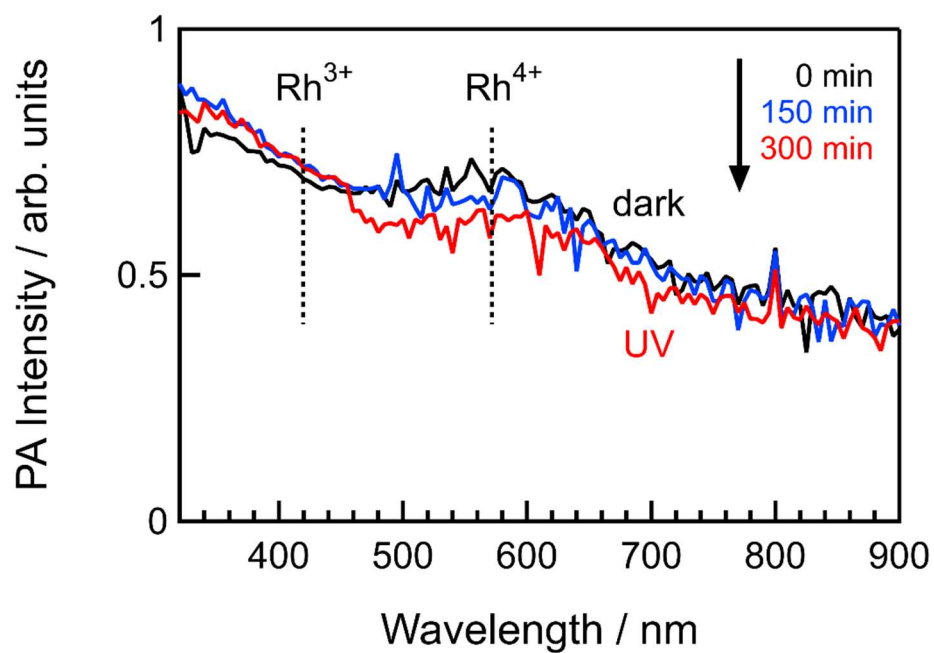
**Fig. S1.** UVVISNIR-PAS spectra of (a) non-doped SrTiO<sub>3</sub> and (b) SrTiO<sub>3</sub>:Rh(1%) under air (upper). Emission spectra of UV light, blue light and red light (lower) and inset figure of emission spectra of LEDs for red light or simultaneous (blue light and red light) irradiation. Samples were prepared at 1373 K for 10 h.



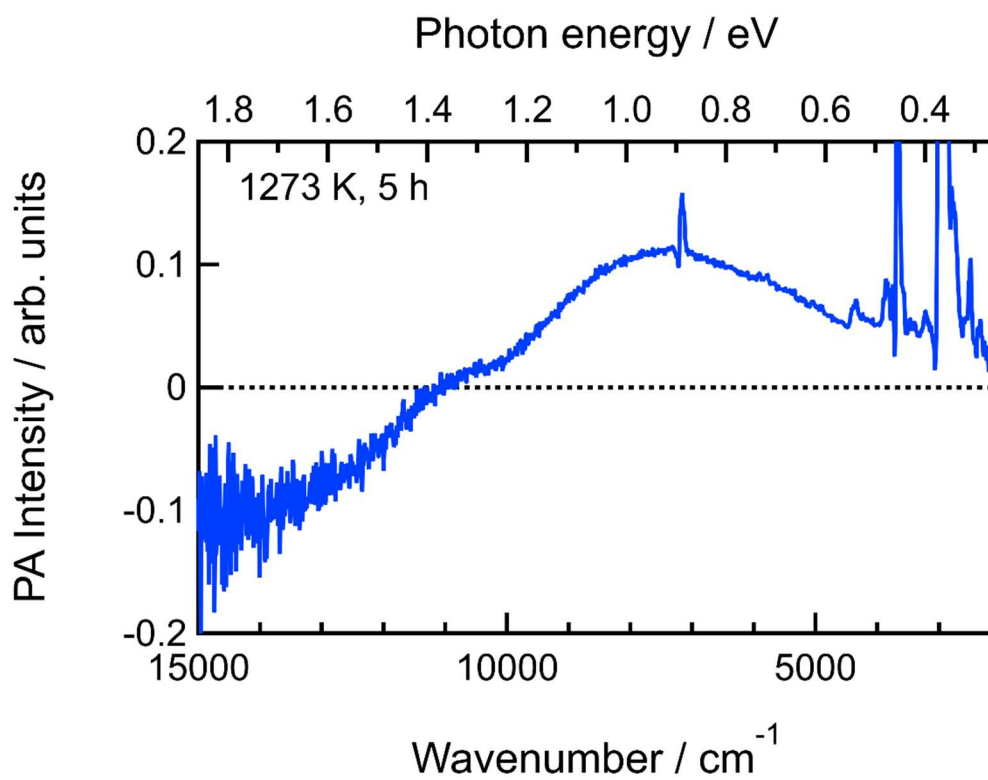
**Fig. S2.** FTIR-PAS spectra of (a) non-doped SrTiO<sub>3</sub> and (b) SrTiO<sub>3</sub>:Rh(1%) under an N<sub>2</sub> atmosphere. Samples were prepared at 1373 K for 10 h.



**Fig. S3.** FTIR-PAS spectra of SrTiO<sub>3</sub>:Rh(1%) without excess Sr under an ethanol-saturated N<sub>2</sub> atmosphere before and during UV irradiation for 140 min. The sample was prepared at 1373 K. Sr0% ex. denotes no addition of excess Sr.

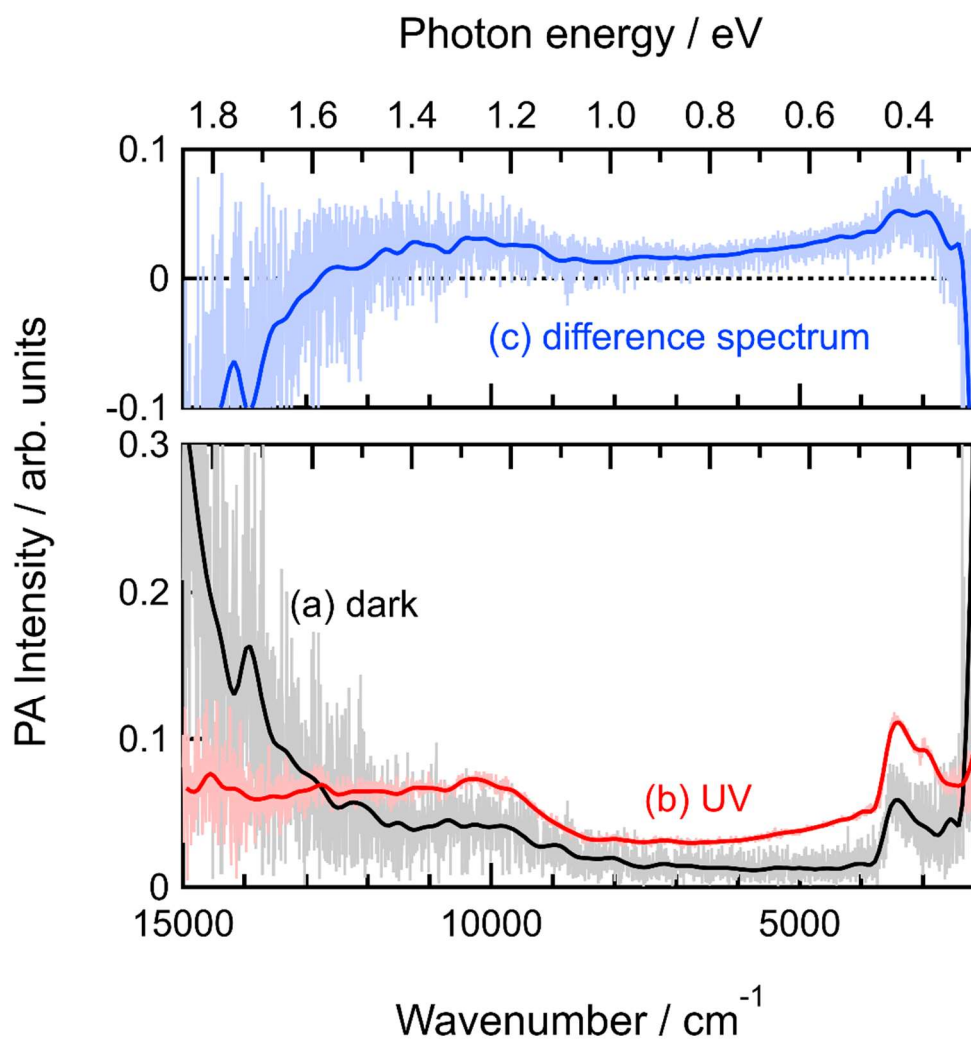


**Fig. S4.** UVVISNIR-PAS spectra of SrTiO<sub>3</sub>:Rh(1%) with adsorbed ethanol under an N<sub>2</sub> atmosphere before and during UV irradiation for 300 min. The sample was prepared at 1373 K.

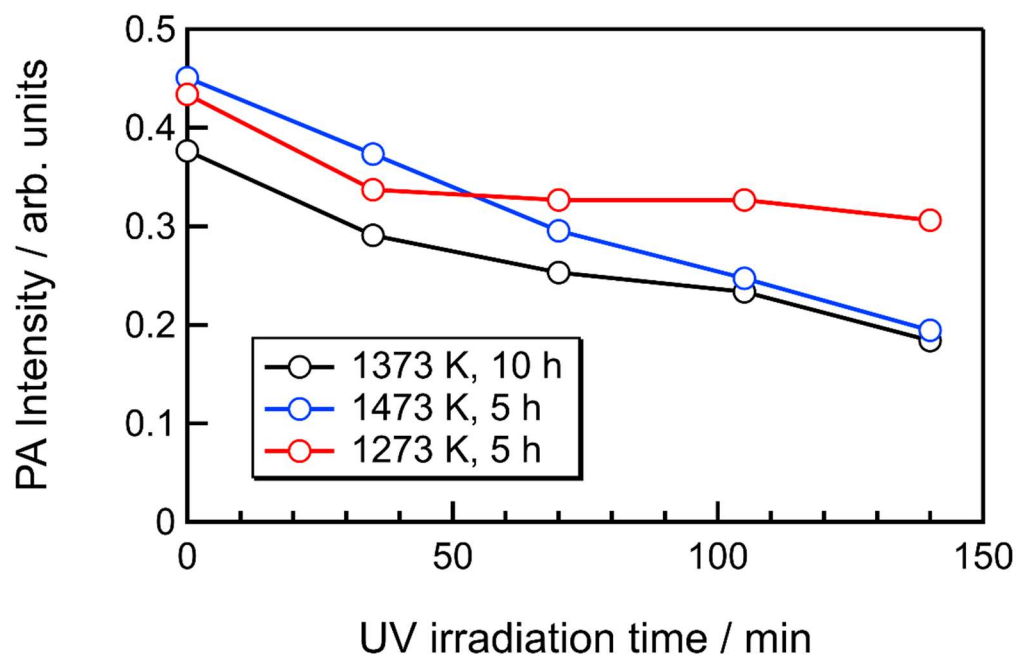


**Fig. S5.** Difference spectrum of SrTiO<sub>3</sub>:Rh(1%) prepared at 1273 K. The spectrum was obtained by the difference in FTIR-PAS spectra before and after UV irradiation for 140 min.

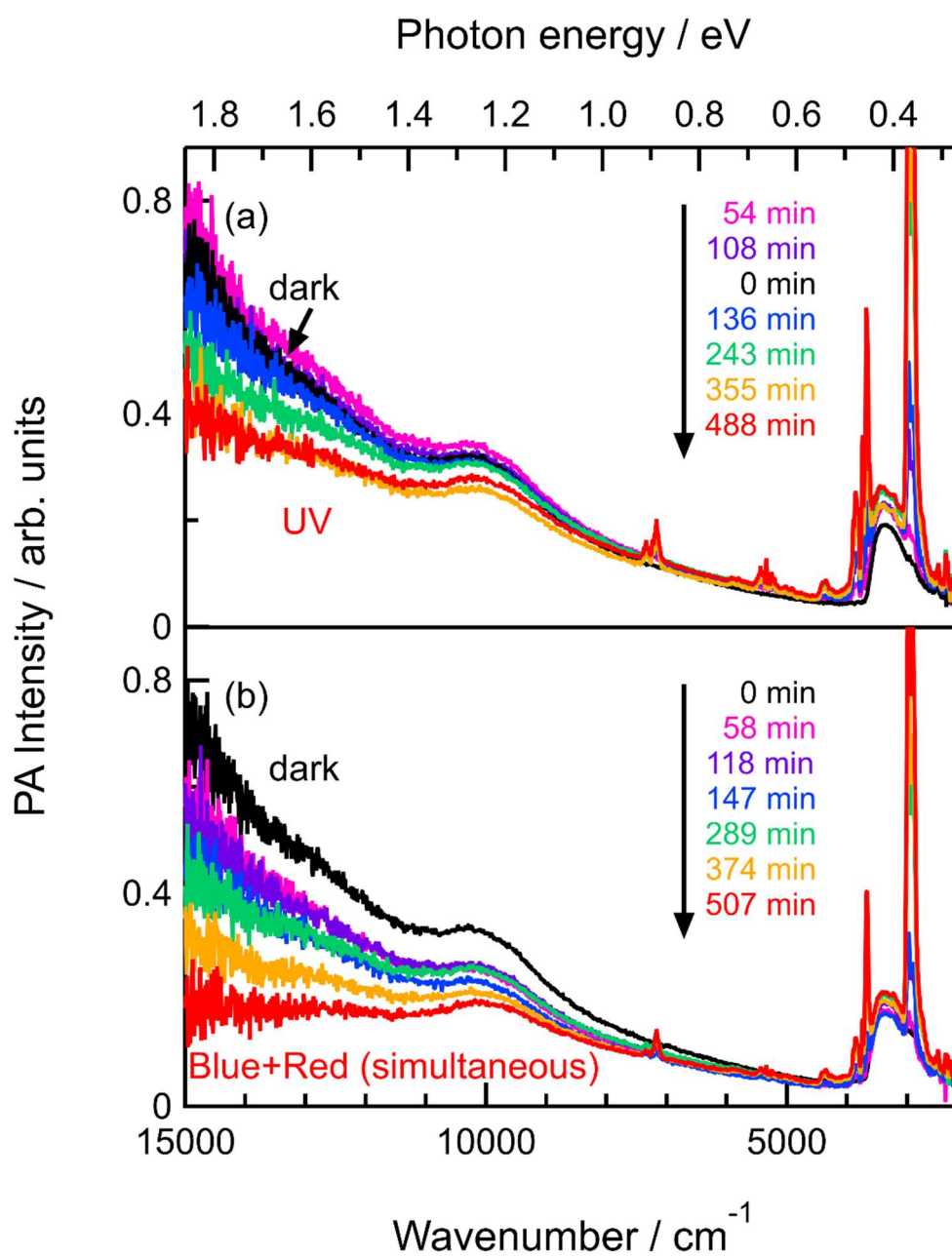




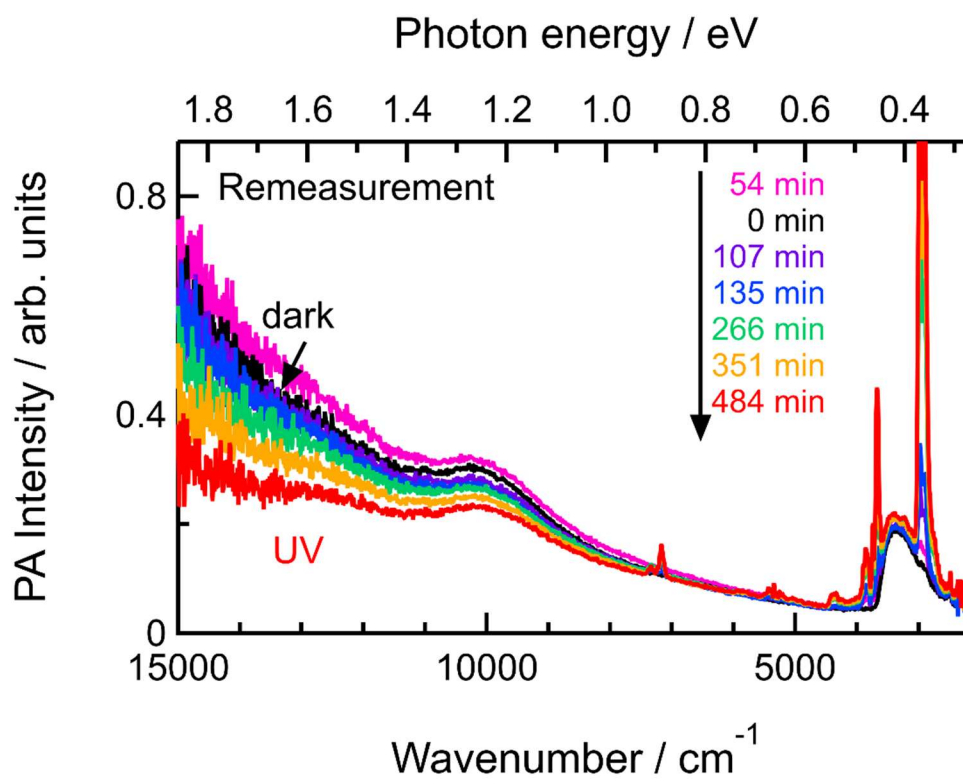
**Fig. S6.** FTIR-PAS spectra of non-doped SrTiO<sub>3</sub> with adsorbed ethanol under an N<sub>2</sub> atmosphere (a) before and (b) after UV irradiation and (c) difference spectrum between (a) and (b). For the measurement, an excess amount of ethanol was removed because sharp peaks attributed to ethanol overlap in the spectrum of SrTiO<sub>3</sub> and it is difficult to observe a subtle absorption due to electron accumulation.



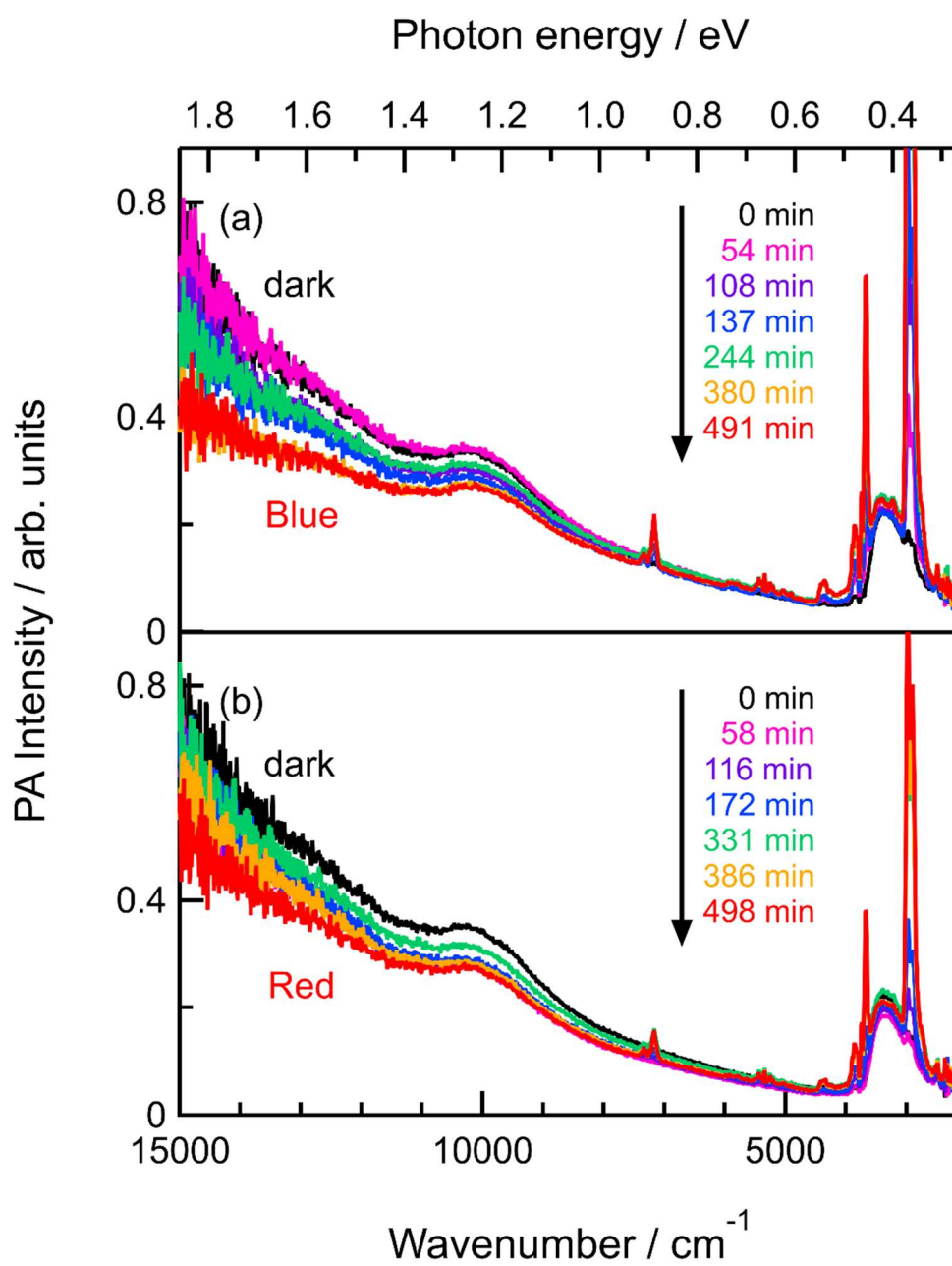
**Fig. S7.** Decrease in PA intensity of SrTiO<sub>3</sub>:Rh(1%) at 13712 cm<sup>-1</sup> under an ethanol-saturated N<sub>2</sub> atmosphere during UV irradiation.



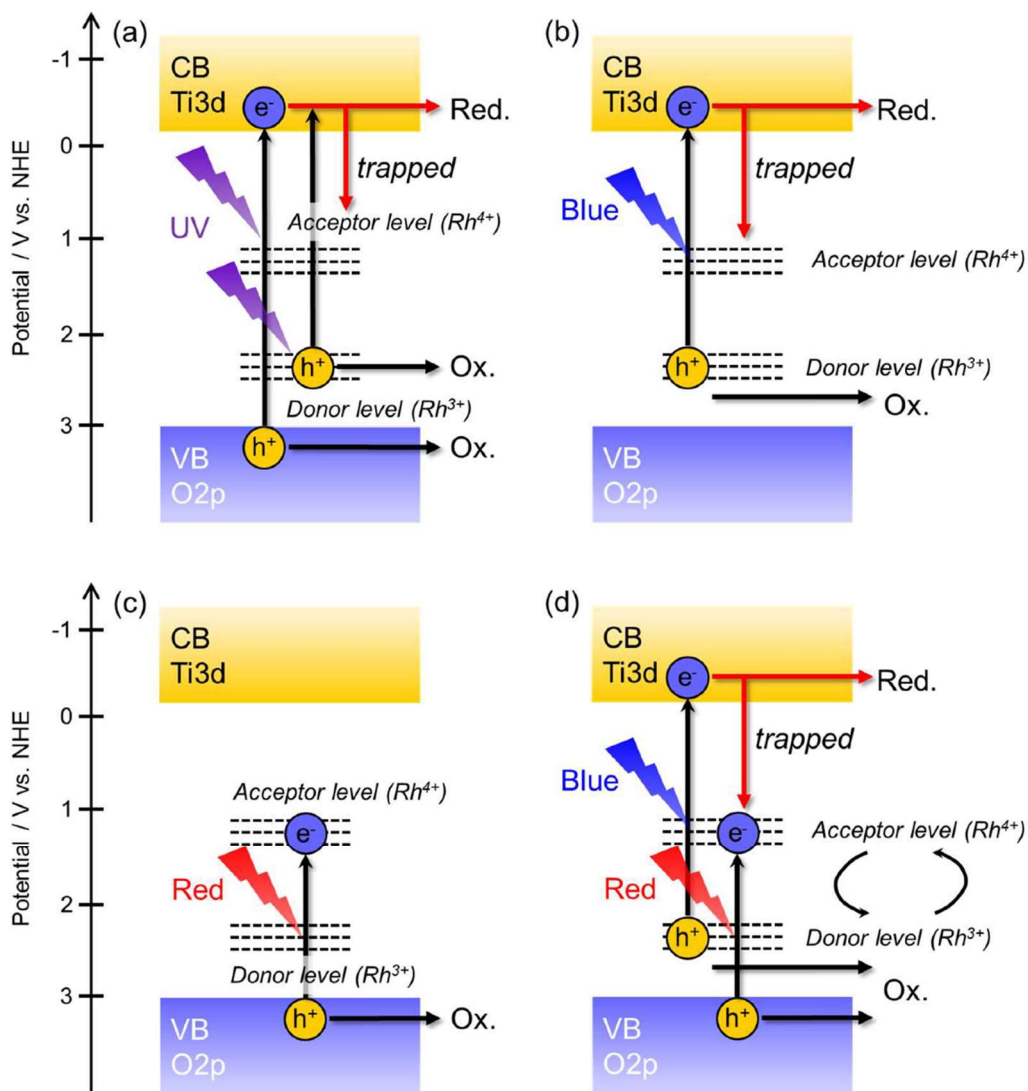
**Fig. S8.** FTIR-PAS spectra of SrTiO<sub>3</sub>:Rh(1%) (prepared at 1373 K) with adsorbed ethanol under an N<sub>2</sub> atmosphere. The sample was photoexcited by irradiation with (a) UV light (365 nm) and (b) blue + red light (455 + 625 nm) for *ca.* 500 min.



**Fig. S9.** FTIR-PAS spectra of SrTiO<sub>3</sub>:Rh(1%) with adsorbed ethanol under an N<sub>2</sub> atmosphere before and during UV irradiation for *ca.* 500 min. The sample was used after atmospheric exposure for 8 days from the end of the last measurement.



**Fig. S10.** FTIR-PAS spectra of SrTiO<sub>3</sub>:Rh(1%) (prepared at 1373 K) with adsorbed ethanol under an N<sub>2</sub> atmosphere. The sample was photoexcited by irradiation with (a) blue light (455 nm) or (b) red light (625 nm) for *ca.* 500 min.



**Fig. S11.** Proposed electron-transfer mechanism of SrTiO<sub>3</sub>:Rh under irradiation with (a) UV light, (b) blue light, (c) red light and (d) blue + red light.

**Table S1.** H<sub>2</sub> evolution over SrTiO<sub>3</sub>:Rh photocatalysts from an aqueous methanol solution under visible-light irradiation

Sample	Preparation condition	Activity / $\mu\text{mol h}^{-1}$
SrTiO <sub>3</sub> :Rh(1%)	SSR (Sr7% ex., 1173K-1h, 1373K-10h)	120
SrTiO <sub>3</sub> :Rh(1%)	SSR (Sr7% ex., 1173K-1h, 1473K-5h)	130
SrTiO <sub>3</sub> :Rh(1%)	SSR (Sr7% ex., 1173K-1h, 1273K-5h)	18

Photocatalyst: 0.3 g, cocatalyst: Pt 0.3 wt% (*in situ* photodeposition), reactant solution: 10 vol% aqueous methanol solution (120 mL), light source: 300 W xenon lamp with a long-pass filter ( $\lambda > 420$  nm).