

Electronic Supplementary Information

**Photoinduced H-aggregation of cationic dyes on metal-oxide surfaces
via light activated molecular migration**

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Here, we describe the following experimental results and the energy level diagram:

- (i) Excitation intensity dependence of the H-aggregation of methylene blue (MB) on TiO₂
- (ii) Light irradiation effects on MB in solution
- (iii) Metal-oxide dependence of photoinduced H-aggregation of MB
- (iv) Light irradiation effects on toluidine blue (TB) on TiO₂
- (v) Energy level diagram of TiO₂, ZnO, MB, and TB
- (vi) Thermal heating effects on MB on TiO₂

Experimental

We purchased MB chloride and ZnO nanoparticles (particle size: ca. 20 nm) from Wako Pure Chemical Industries, TB chloride from Tokyo Chemical Industry, and TiO₂ (rutile) nanoparticles (particle size < 100 nm), SiO₂ nanoparticles (particle size: ca. 15 nm), and Al₂O₃ nanoparticles (particle size < 50 nm) from Sigma-Aldrich. We obtained TiO₂ (anatase) nanoparticles (particle size: ca. 20 nm) from Aerosil. MB-adsorbed metal-oxide nanoparticles were prepared by immersing metal-oxide nanoparticles (0.1 g) into the acetone solution (10 mL) of 6 μM MB chloride for 30 min, filtering and washing the immersed nanoparticles to remove unadsorbed MB, and then vacuum-drying them. TB-adsorbed TiO₂ (anatase) nanoparticles were prepared in a similar manner using acetonitrile as solvent. Light irradiation and measurements of absorption and diffuse reflection spectra were carried out in a similar way described in the present paper.

Results and discussion

(i) Excitation intensity dependence of the H-aggregation of MB on TiO₂

We examined the excitation intensity dependence of the H-aggregation of MB adsorbed on TiO₂ (anatase). Fig. S1(a) and (b) show Kubelka-Munk function spectra of MB/TiO₂ (anatase) before and after the red light irradiation (λ : 650 nm) with two excitation intensities of 0.38 mW/cm² and 1.14 mW/cm², respectively. The adsorption density (ca. 2×10^{11} cm⁻²) of MB of the samples is the same as that used in the experiment shown in Fig. 3(a). The spectral changes upon the light irradiation became slower with decreasing the excitation light intensity. The detail of the analysis of the excitation intensity dependence is described in the main text.

(ii) Light irradiation effects on MB in solution

Fig. S2(a) and (b) show the absorption spectra of 0.1 mM and 0.01 mM MB chloride aqueous solutions before and after red light irradiation (λ : 650 nm, I_{ex} : 3.8 mW/cm²), respectively. These spectra were measured using quartz cells with the optical path length of (a) 1 mm and (b) 1 cm. For the higher concentration sample, the MB monomer and dimer bands were observed at 665 nm and 611 nm, respectively. Upon the light irradiation, no remarkable spectral changes were observed with slight decrease of the monomer and dimer peaks. For the lower concentration sample, only the monomer band was observed at 665 nm showing almost no light irradiation effects. We carried out a similar experiment for MB chloride acetone solutions of the two concentrations. As shown in Fig. S3(a) and (b), the MB monomer peak at 657 nm showed almost no light irradiation effects for both the concentrations.

(iii) Metal-oxide dependence of photoinduced H-aggregation of MB

Fig. S4(a)-(d) show Kubelka-Munk function spectra of MB/TiO₂ (rutile), MB/ZnO, MB/SiO₂, and MB/Al₂O₃ before and after red light irradiation (λ : 650 nm, I_{ex} : 3.8 mW/cm²),

respectively. In MB/TiO₂ (rutile) and MB/ZnO, photoinduced H-aggregation was observed. Particularly, in MB/ZnO the oligomer band was observed at 537 nm, showing larger blue-shift than that (543 nm) in MB/TiO₂ (anatase). This result indicates that MB readily forms H-aggregates on ZnO surfaces as compared to TiO₂ (anatase) and TiO₂ (rutile) surfaces. On the other hand, in MB/SiO₂ and MB/Al₂O₃ the monomer band was weakly blue-shifted even by the light irradiation for 2 hours. The small light irradiation effect is considered to be due to stronger MB-surface interactions in SiO₂ and Al₂O₃ than in TiO₂ (rutile) and ZnO, which may suppress the photoactivated migration of MB monomers and the resultant H-aggregate formation. These results indicate that the photoinduced H-aggregation of MB also take place on the other metal-oxide surfaces than TiO₂ (anatase) and the aggregation rate depends on the strength of MB-metal oxide interactions.

(iv) Light irradiation effects on TB on TiO₂

Fig. S5 shows Kubelka-Munk function spectra of TB/TiO₂ (anatase) before and after red light irradiation (λ : 630 nm). The monomer band at 633 nm was blue-shifted by the red light irradiation and two absorption bands appeared at 602 and 550 nm after the 2 min light irradiation. According to the literature, the absorption bands at 602 and 550 nm are assigned to the dimer and trimer of TB, respectively.¹ Accordingly, photoinduced H-aggregation also occurs for TB.

(v) Energy level diagram of TiO₂, ZnO, MB, and TB

Fig. S6 shows the energy level diagram of the conduction-band edges of TiO₂ (anatase) and ZnO and the LUMO levels of MB and TB.²⁻⁶ The LUMO levels of MB and TB lie below the conduction band edges of TiO₂ and ZnO. This diagram indicates that electron injection from the S₁ states of MB and TB into the conduction bands of TiO₂ and ZnO hardly occurs.

(vi) Thermal heating effects on MB on TiO₂

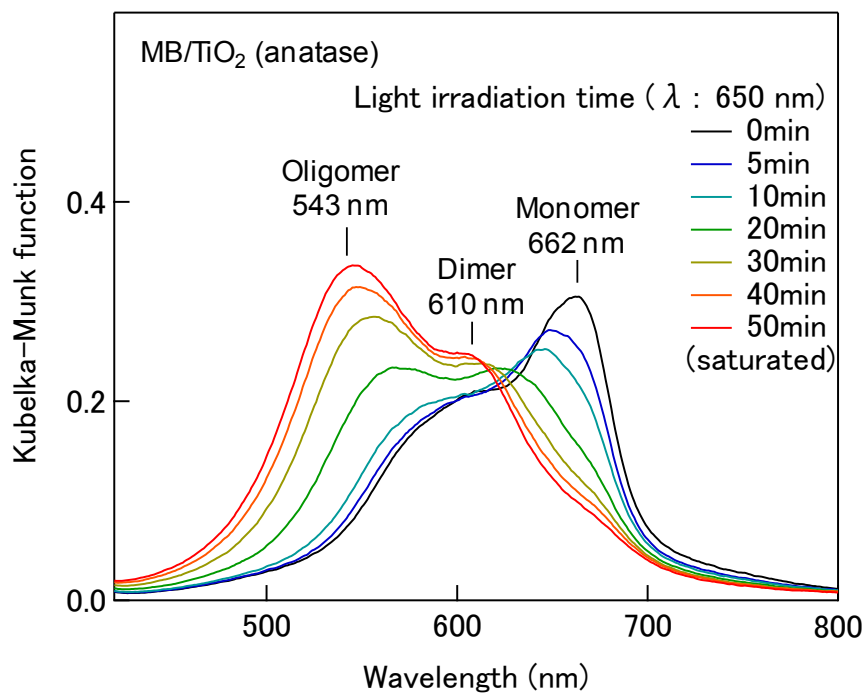
We examined thermal heating effects on MB adsorbed on TiO₂ (anatase) at several temperatures. The Kubelka-Munk function spectrum of MB/TiO₂ was hardly changed by heating at temperatures below ca. 75°C. Heating the sample at 80°C caused the blue-shift of the monomer band to 610 nm indicative of the dimer formation and also produced a broad absorption band between 400 and 900 nm, as shown in Fig. S7(a). Increasing the heating temperature to 100°C or higher temperatures decreased the dimer band and increased the broad absorption, as shown in Fig. S7(b). In addition, the colour of MB/TiO₂ was changed from blue to pale yellow by heating at 100°C. These results indicate that MB was decomposed by heating ca. 100°C or higher temperatures due to the thermally activated catalytic ability of TiO₂.

Fig. S8(a) and (b) show the Kubelka-Munk function spectra of MB/TiO₂ after heating at 80°C and 100°C, respectively. In contrast to the photogenerated H-aggregates, the dimer band did not return to the initial monomer state under the dark condition even after several days. This result indicates that the thermally formed dimer may be different from the photoinduced H-aggregates.

References

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(a) Excitation light intensity: 0.38 mW/cm²



(b) Excitation light intensity: 1.14 mW/cm²

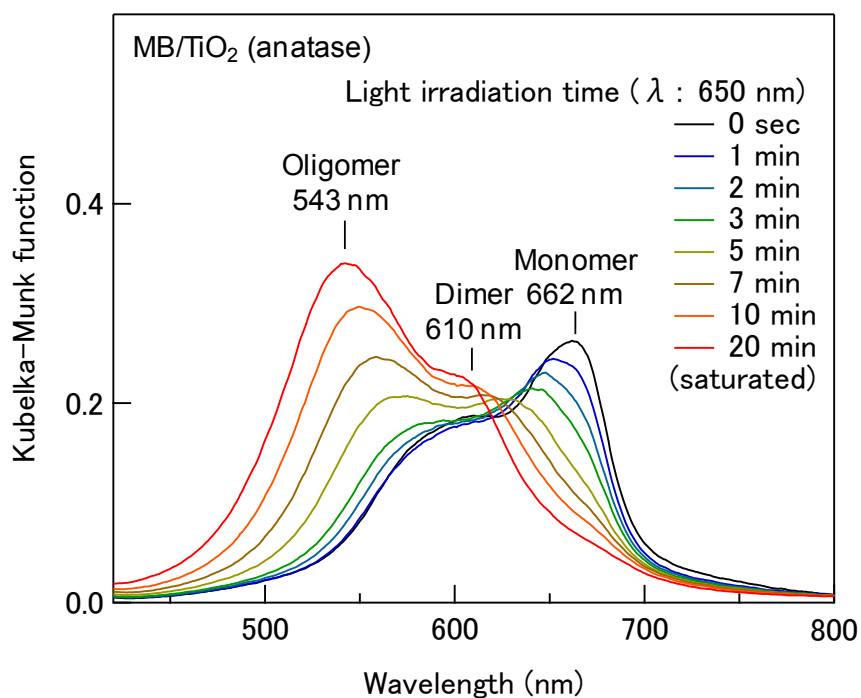


Fig. S1 Kubelka-Munk function spectra of MB/TiO₂ (anatase) (adsorption density: ca. 2×10^{11} cm⁻²) before and after red light irradiation (λ : 650 nm) with excitation light intensity of (a) 0.38 mW/cm² and (b) 1.14 mW/cm².

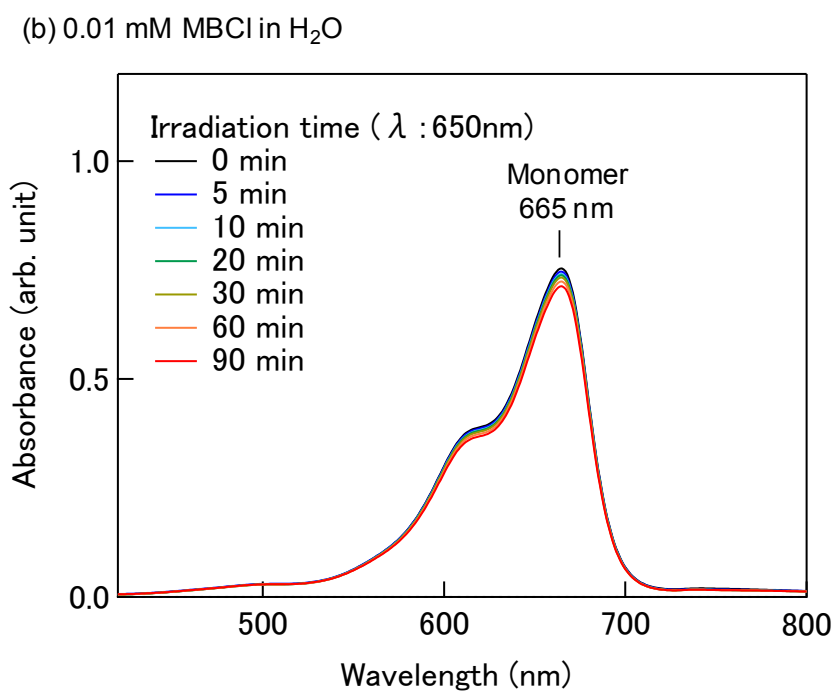
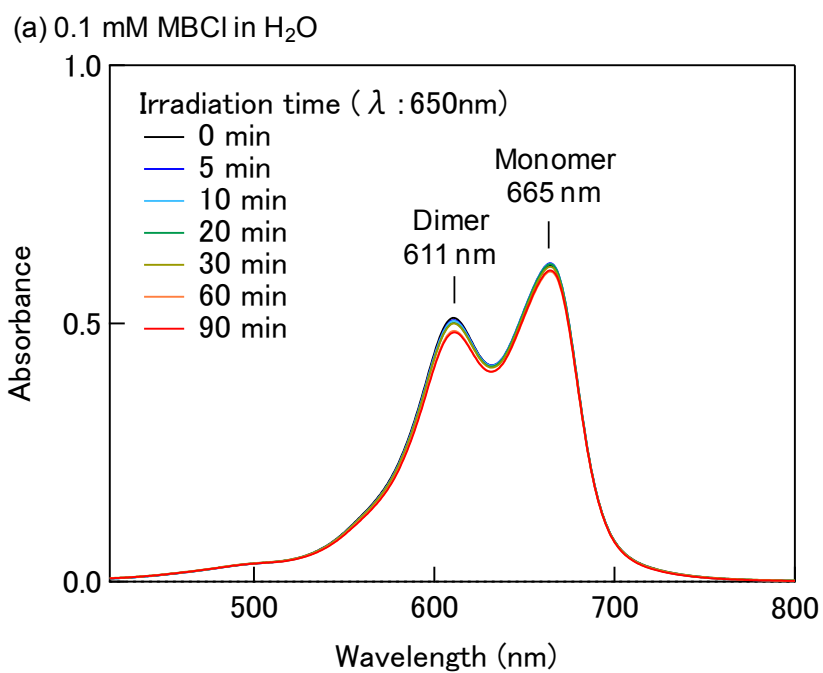
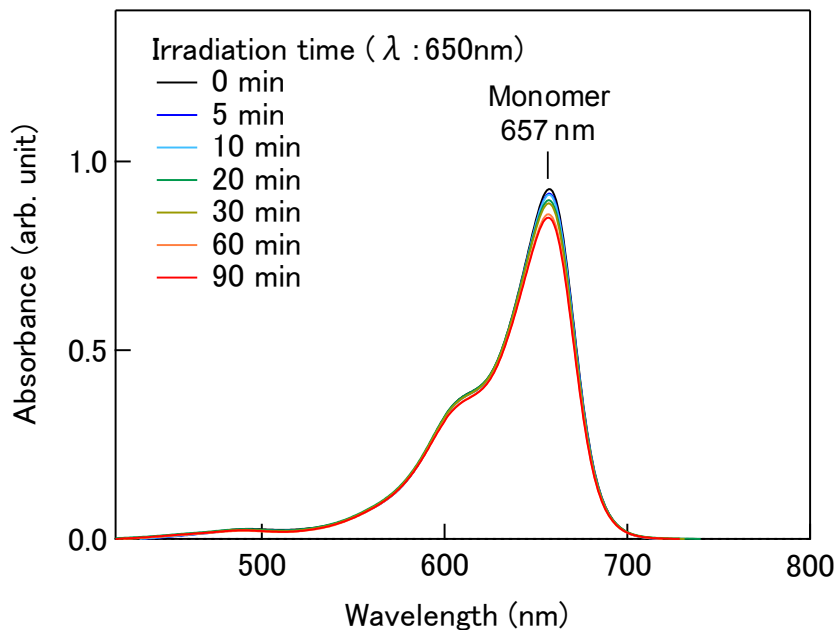


Fig. S2 Absorption spectra of (a) 0.1 mM MBCl in aqueous solution and (b) 0.01 mM MBCl in aqueous solution before and after red light irradiation (λ : 650 nm, I_{ex} : 3.8 mW/cm²). The absorption spectra in (a) and (b) were measured using quartz cells with the optical path length of 1 mm and 1 cm, respectively.

(a) 0.1 mM MBCI in acetone



(b) 0.01 mM MBCI in acetone

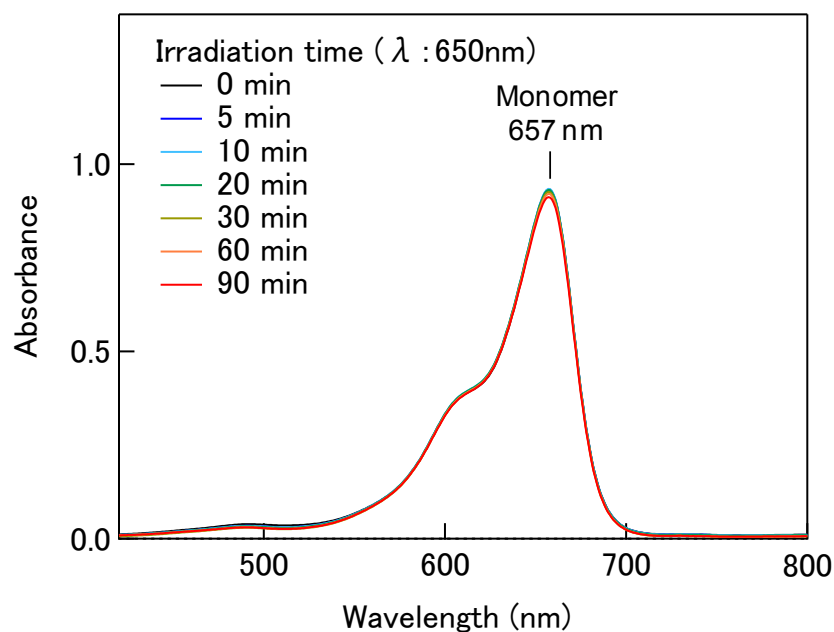


Fig. S3 Absorption spectra of (a) 0.1 mM MBCI in acetone solution and (b) 0.01 mM MBCI in acetone solution before and after red light irradiation (λ : 650 nm, I_{ex} : 3.8 mW/cm²). The absorption spectra in (a) and (b) were measured using quartz cells with the optical path length of 1 mm and 1 cm, respectively.

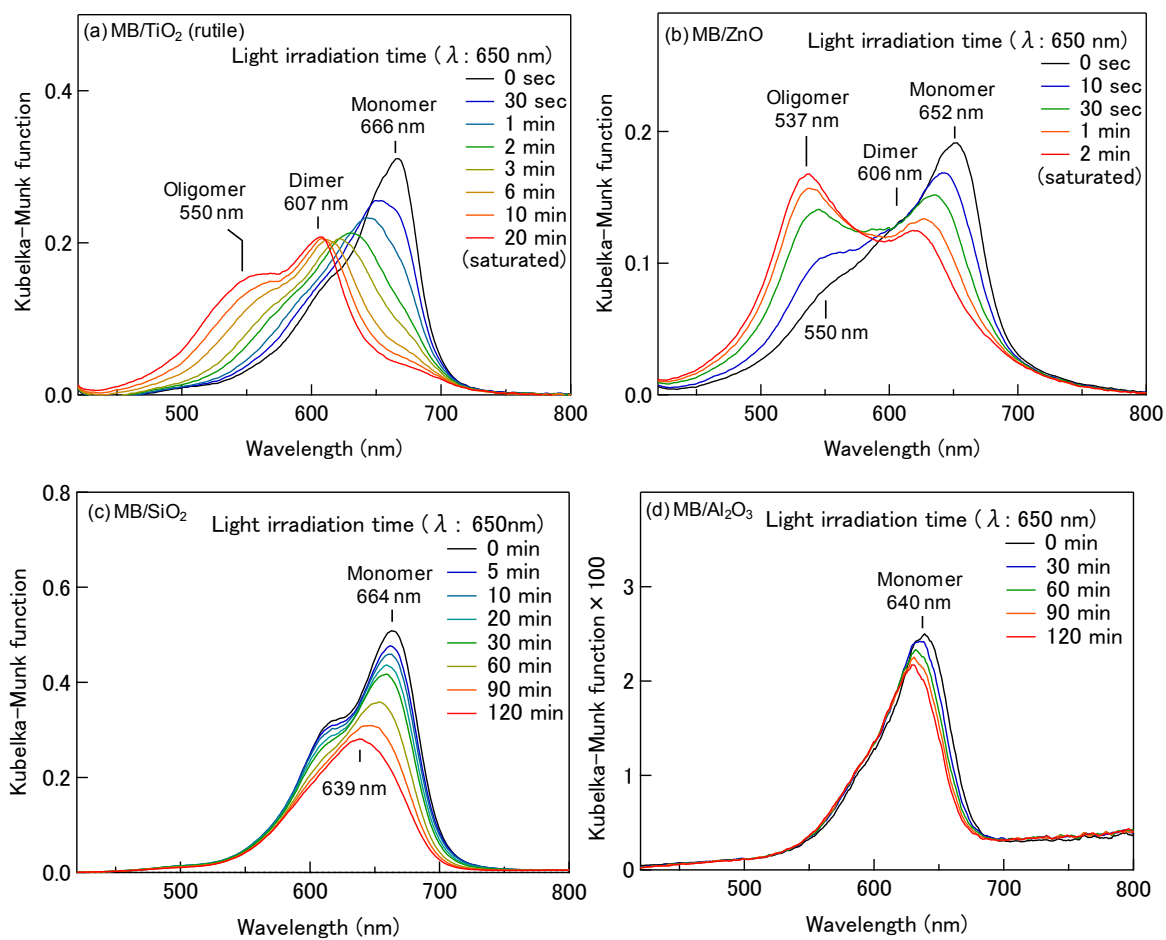


Fig. S4 Kubelka-Munk function spectra of (a) MB/TiO₂ (rutile), (b) MB/ZnO, (c) MB/SiO₂, and (d) MB/Al₂O₃ before and after red light irradiation (λ : 650 nm, I_{ex} : 3.8 mW/cm²).

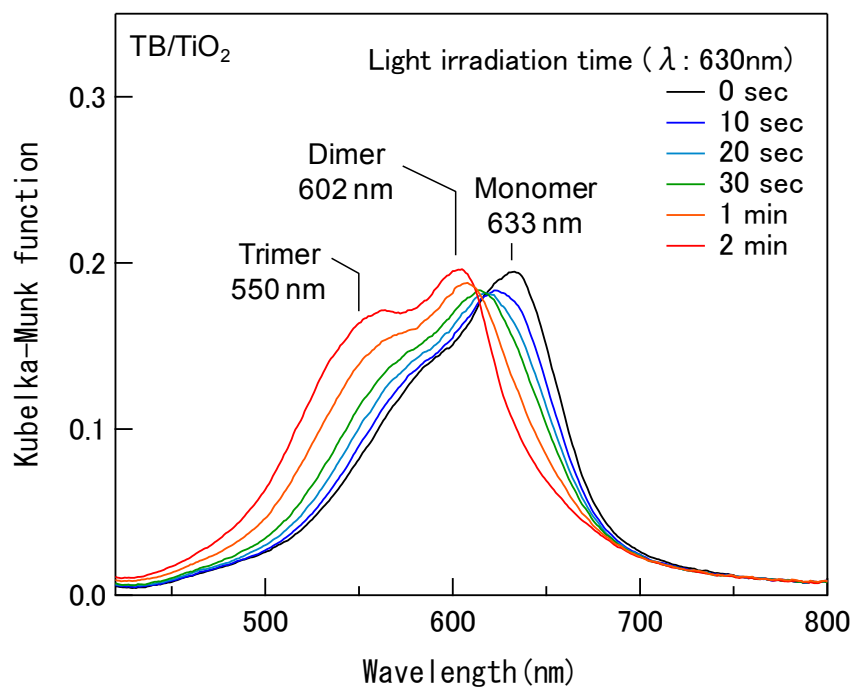


Fig. S5 Kubelka-Munk function spectra of TB/TiO₂ (anatase) before and after red light irradiation (λ: 630 nm).

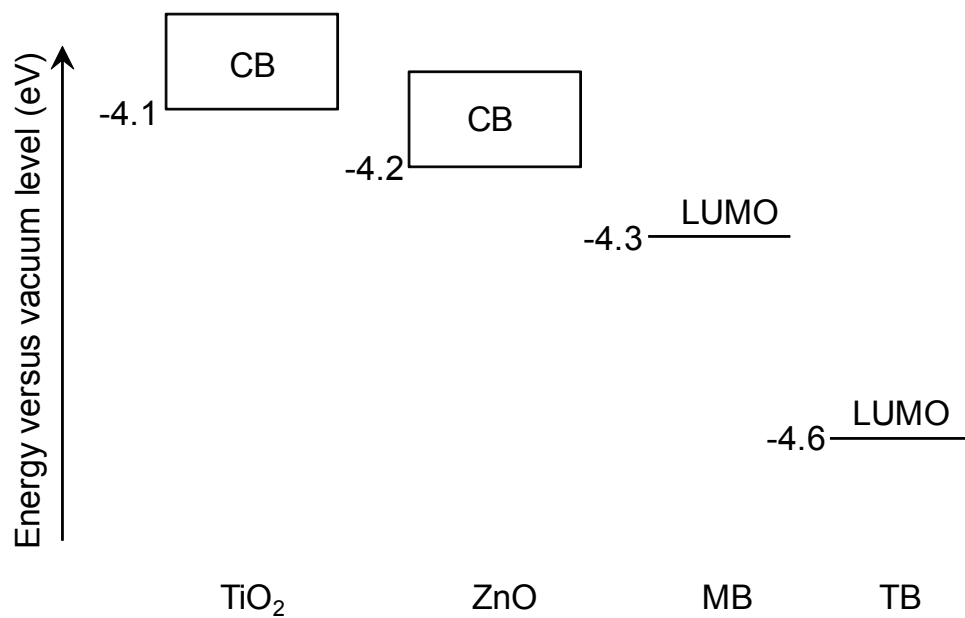


Fig. S6 Energy level diagram of the conduction-band edges of TiO₂ (anatase) and ZnO and the LUMO levels of MB and TB.

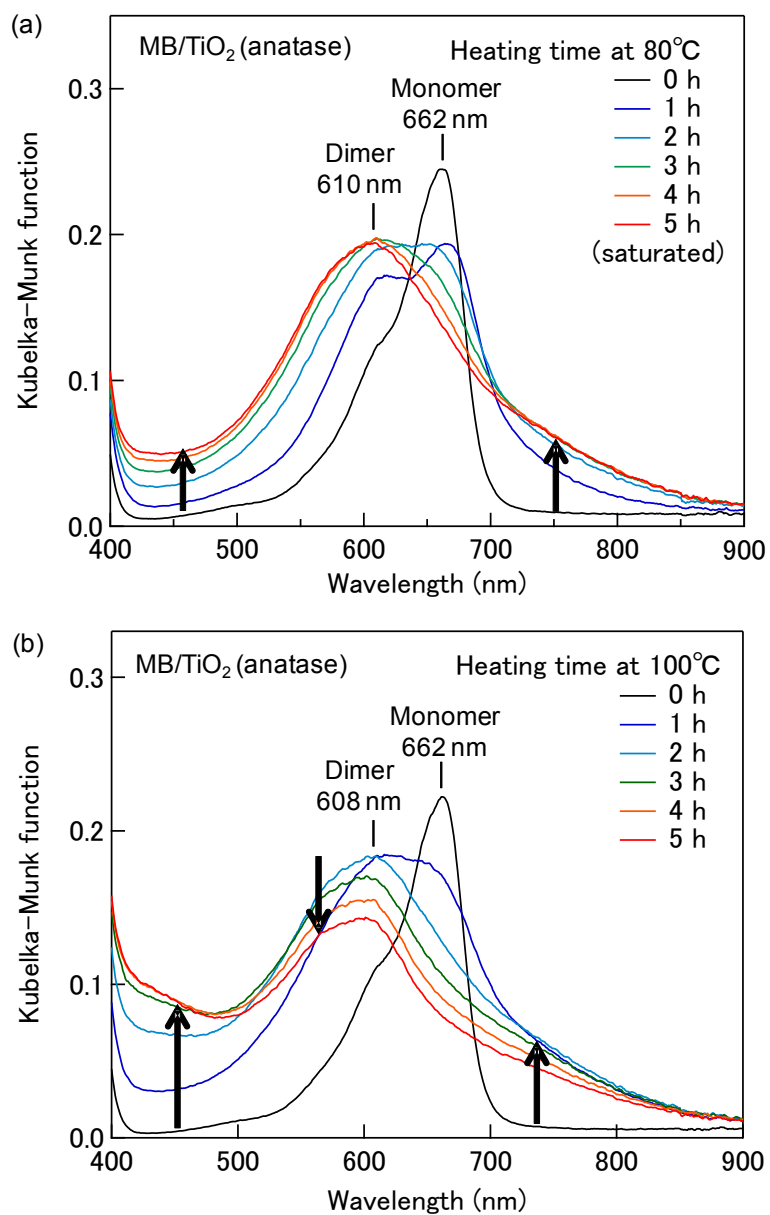


Fig. S7 Kubelka-Munk function spectra of MB/TiO₂ (anatase) (adsorption density: ca. 2×10^{11} cm⁻²) before and after heating at (a) 80°C and (b) 100°C in the dark.

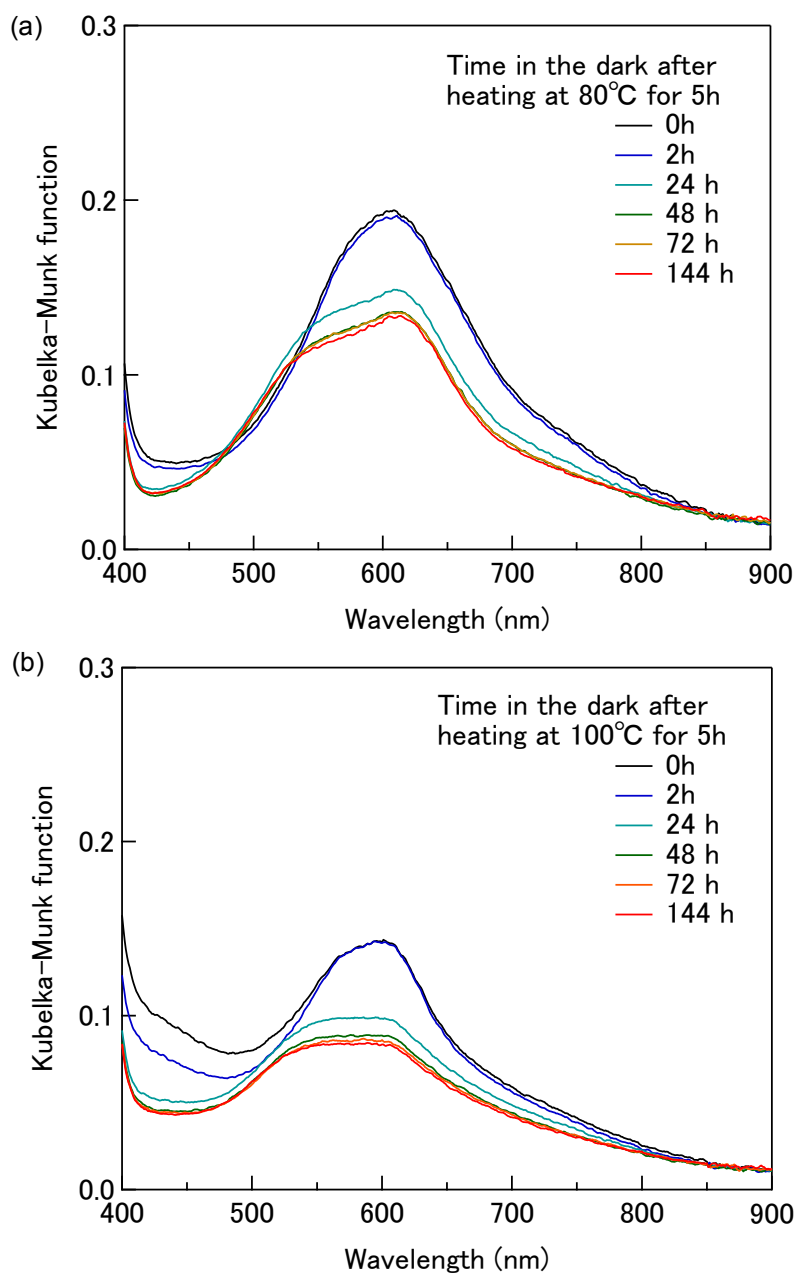


Fig. S8 Temporal changes of Kubelka-Munk function spectra of MB/TiO₂ (anatase) under the dark condition at room temperature after heating at (a) 80°C and (b) 100°C for 5 hours.