

## Supplementary Information for

### Novel Accumulation of Photo-Induced $MV^{+•}$ Embedded in a $TiO_2$ Shell and Discharge of Electrons to a Pt Electrode

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#### Experimental Details

##### Absorption spectra, ESR spectra of $MV^{2+}$ @ $TiO_2$ and its time course

Fig. 1S shows the ESR spectra of  $MV^{2+}$  @  $TiO_2$  aqueous dispersion with irradiation time of a 500-W Xenon lamp. The typical ESR signals of  $MV^{+•}$  ( $g=2.003$ ) were observed from 1 to 4 min of the irradiation. These data were used to plot of Fig. 3S.

Fig. 2S shows the absorption spectra of  $MV^{2+}$  @  $TiO_2$  aqueous suspension before irradiation, at 0 min of irradiation, and 33min after irradiation by a 500-W-

high-pressure mercury lamp. The typical absorption peaks of  $MV^{+\bullet}$  were observed at 395 nm and 600 nm.

Fig. 3S shows the time dependence of the  $MV^{+\bullet}$  concentration under continuous UV irradiation.  $MV^{+\bullet}$  is produced in both dispersion systems by electron transfer from the UV-irradiated  $TiO_2$  to  $MV^{2+}$ . The concentration increases more rapidly in  $MV^{2+}@TiO_2$  than in  $\square@TiO_2/MV^{2+}$ . This is due to the longer lifetime of  $MV^{+\bullet}$  in  $MV^{2+}@TiO_2$  (Fig. 3 in the text) probably because more radical cations are stored in a short period of time under the same irradiation condition in this dispersion. The increase in  $MV^{+\bullet}$  concentration slows at 1-4 min of irradiation in this dispersion presumably because of bimolecular self-quenching of the radical cation at high concentration. Since no absorption of  $MV^{2+}$  is observed for this dispersion after 4 min, the decrease in  $MV^{+\bullet}$  concentration in this time region of Fig. 3S is due to the decomposition of the radical cation. The time course of  $MV^{+\bullet}$  concentration observed for  $MV^{2+}@TiO_2$  is also observed for  $\square@TiO_2/MV^{2+}$ , although bimolecular quenching of the radical cation is absent because of the low concentration of the radical cation before decomposition.

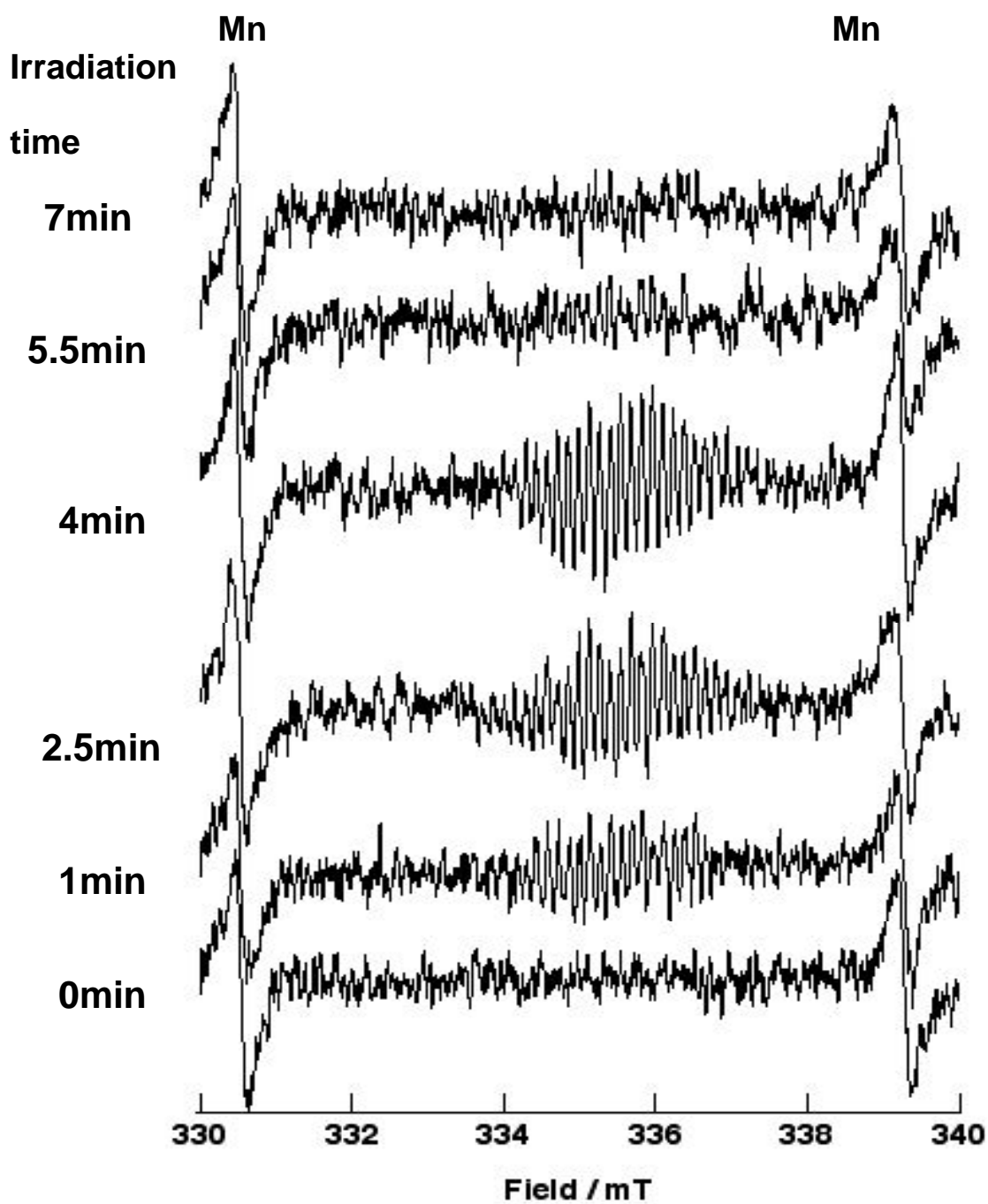


Fig. 1S ESR spectra of  $MV^{2+}$  @ $TiO_2$  aqueous dispersion with Mn as a standard material during by a 500-W Xe lamp by using JEOL TE-300. Field modulation:  $79\mu T$ , Power: 8mW

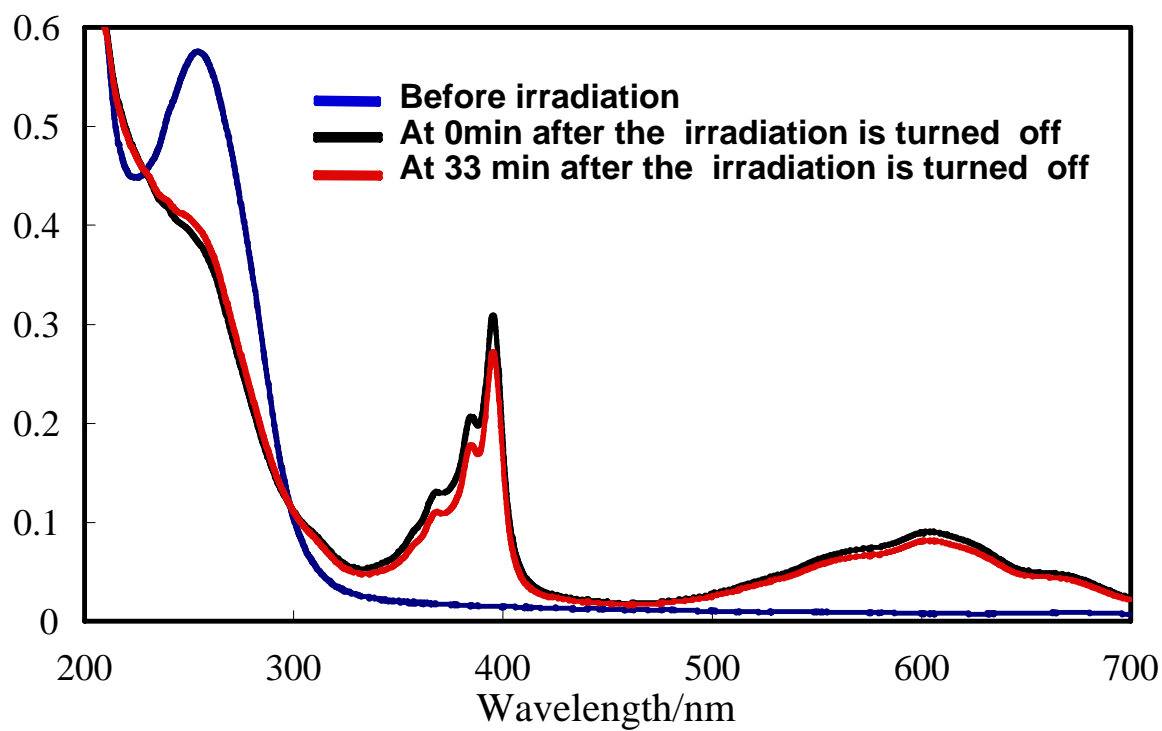


Fig. 2S Absorption spectra of MV<sup>2+</sup> @TiO<sub>2</sub> aqueous dispersion before irradiation, at 0 min of irradiation, and 33min after irradiation by a 500-W-high-pressure mercury lamp.

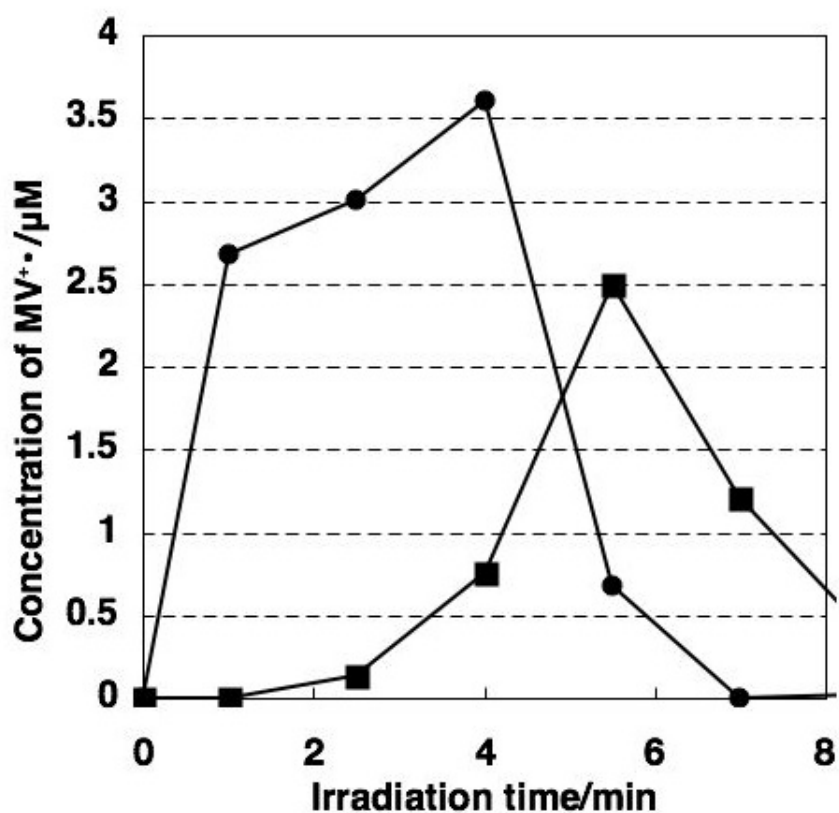


Fig. 3S Time dependence of MV<sup>•+</sup> concentration in aqueous dispersion of MV<sup>2+</sup> @ TiO<sub>2</sub> (●) and in mixed aqueous dispersion of □ @ TiO<sub>2</sub>/MV<sup>2+</sup> (■) under the continuous UV irradiation by a filtered 500W Xe lamp. Concentration is calculated from the peak area at g=2.003.<sup>1</sup> ESR spectra were obtained by a JEOL TE-300 spectrometer.

## References

- 1 A. E. Kaifer and A. J. Bard, *J.Phys.Chem.*, 1985, **89**, 4876.