Supplementary Material (ESI) for PCCP

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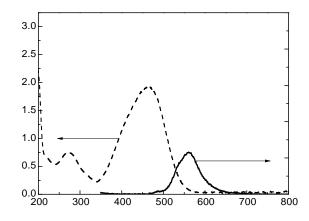
Electronic supplementary information

## The Degradation Mechanism of Methyl Orange Under Photo-Catalysis of $TiO_2$

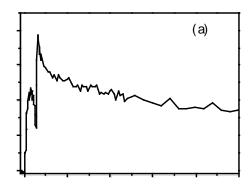
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**Fig. S1** UV-Vis absorption spectrum (dot profile) and fluorescence emission spectrum (solid profile) for MO in water  $10^{-4}$  M.



**Fig. S2** (a) TA Decay profile of  $TiO_2$  bulk film in MO MeCN solution. (b) TA Decay profile of MO solution in MeCN. Pump by 267 nm, probe at 675nm.



Description of the method used to obtain the TA decay profile of  $TiO_2$  holes in MO solution (i.e. the enhanced solid profile in Fig. 7) investigated in the paper.

As mentioned in the body text, MO has a weak transient absorption at 675 nm whose onset and maximum are at 0.7 ps and 2.3 ps, earlier than the TA onset time (3.0 ps) of the bulk TiO<sub>2</sub> film. In order to get rid of the TA contribution from MO, the TA decay values of the bulk TiO<sub>2</sub> film in MO solution should be subtracted by the MO TA decay values scaled by an appropriate factor. In Fig. S2 (a), the TA peak at about 2.3 ps corresponds to the TA of MO which appears in Fig. S2 (b), and the TA peak at about 3.5 ps corresponds to the TA of TiO<sub>2</sub> holes. In order to obtain the TA decay profile of bulk TiO<sub>2</sub> film in MO solution (i.e. the enhanced solid profile in Fig. 7), Delta OD values in Fig. S2 (a) need to be subtracted by Delta OD values in Fig. S2 (b) scaled by 0.69.