

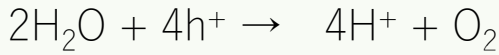
Multielectron-transfer processes in photocatalytic oxygen evolution on titania: Light intensity-dependence study

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Photocatalytic multi-electron (hole) reaction

in the presence of electron acceptor (Ag^+ , Fe^{3+} , IO_3^-)



for improving multi-electron reaction efficiency

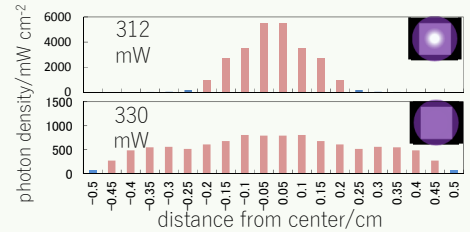
- charge separation
- recombination
- reaction mechanism

Another photon absorption during the lifetime of hole → Depending on the light intensity (photon density)?

NS Lighting(NSL)
focused light

Hamamatsu
Photonics(HM
P)

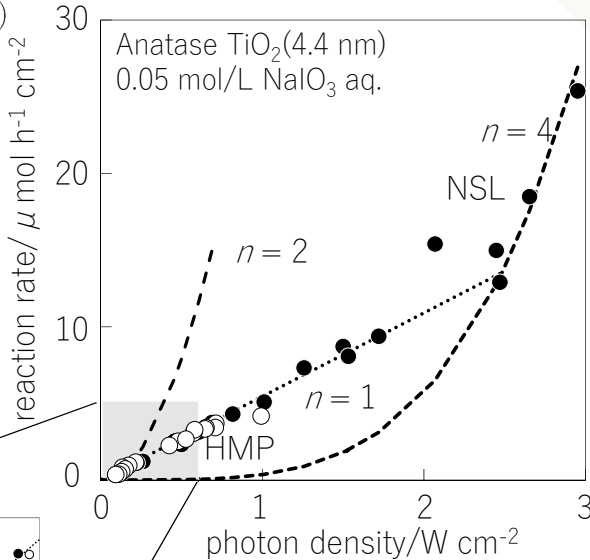
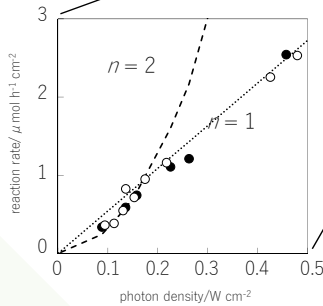
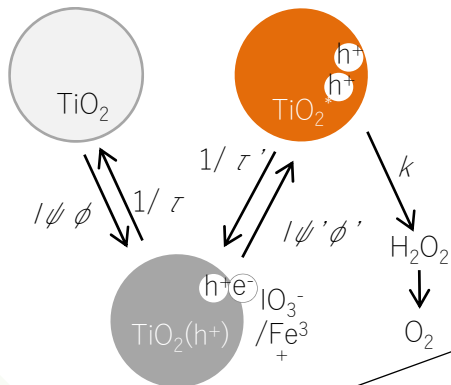
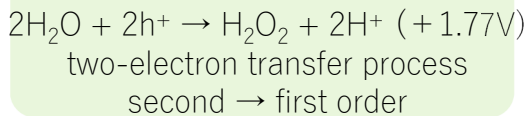
Unfocused light



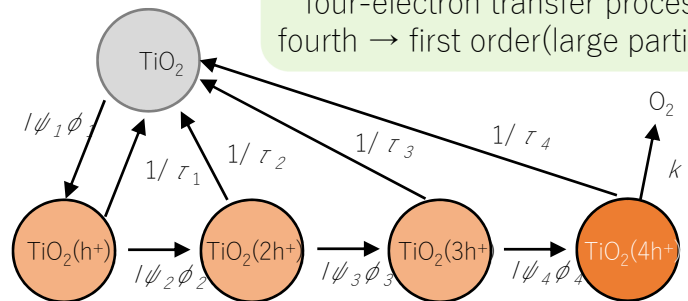
Analysis of light-intensity (photon density) dependence for multi-electron transfer mechanism

multi-electron reaction rate and mechanism depending on the irradiation photon density

low photon density (NSL, HMP)



high photon density (NSL)
 $2\text{H}_2\text{O} + 4h^+ \rightarrow \text{O}_2 + 4\text{H}^+ (+1.23\text{V})$
four-electron transfer process
fourth → first order (large particle)



kinetic equation from multi-electron model

two-electron transfer process

low light-intensity limit : second order

$$r = \frac{k\psi\psi'\phi\phi'\tau I^2}{(k + 1/\tau)}$$

high light-intensity limit : first order

$$r = \psi\phi I$$

four-electron transfer process

low light-intensity limit : fourth order

$$r = \frac{k\psi_1\psi_2\psi_3\psi_4\phi_1\phi_2\phi_3\phi_4 I^4}{(1/\tau_1 + \psi_2\phi_2)(1/\tau_2 + \psi_3\phi_3)(1/\tau_3 + \psi_4\phi_4)(k + 1/\tau_4)}$$

high light-intensity limit : first order

$$r = \psi_1\phi_1 I \quad (I \gg \gg 1/\tau_1, 1/\tau_2, 1/\tau_3, 1/\tau_4)$$