“Proof of Multi Electron Transfer in Heterogeneous Photocatalysis”

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For heterogeneous photocatalysis, it is well known that photocatalytic oxidation of water into molecular oxygen is induced by particulate photocatalysts in the presence of electron acceptors. This reaction has been presumed to proceed through a four-electron (hole) process, and therefore it is expected that reaction rate depends on light intensity and particle size of photocatalyst, which influence the number of photons absorbed by one photocatalyst particle. However such dependences have rarely been reported and discussed so far. In this study, the author reports light-intensity and particle-size dependences of rate of oxygen evolution from suspensions of commercial titania samples using iodate and iron(III) ions as an electron acceptor under intense UV-LED irradiation (365 nm; < 300 mW). The light-intensity dependence of rate of oxygen evolution from a suspension of rutile (Tayca MT-150A; 13 nm) with iron(III) showed a higher-order non-linear dependence in the relatively lower (< 190 mW = threshold intensity=I(thr)), while the rate was almost proportional to the intensity in the higher intensity range. Such dependence could be reproduced by second and first-order equations, respectively. Similar bimodal dependences, with different I(thr), were also observed when the other titania samples were used in the presence of iodate or iron(III) ions. Assuming a kinetic model in which second-photon absorption by a one photon-absorbing particle (TiO2(h)) within its lifetime leads to oxygen evolution, a rate equation was derived using parameters of lifetime of TiO2(h), secondary photon-absorption efficiency and rate constant of oxygen evolution by a two-photon absorbing particle(TiO2*), and further derivation for lower and higher intensity limits reproduced the bimodal light-intensity dependences. Threshold intensity (I(thr)) at which order of light-intensity dependence formally changes from second to first is defined as intensity for the equal rates of lower and higher limits. Differences in I(thr) depending on the kind of electron acceptors, crystalline structure (anatase or rutile) and particle size are discussed.