

# Multielectron Reduction of Molecular Oxygen in Photocatalysis by Bismuth Tungstate and the Other Metal-oxide Particles

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It has been believed that photocatalytic degradation of organic compounds under aerobic conditions proceeds through one-electron reduction of molecular oxygen to liberate superoxide anion radical especially in the reaction systems in which anatase titania is used as a photocatalyst. As one of the visible-light responsive photocatalysts, flake ball (FB)-shaped bismuth tungstate ( $\text{Bi}_2\text{WO}_6$ : BTO) particles prepared by hydrothermal reaction using bismuth nitrate and sodium tungstate as starting materials [1] exhibit photocatalytic activity for oxidative decomposition of organic compounds comparable to that of commercial titania photocatalysts, while the activity for methanol dehydrogenation is relatively low even with platinum-loaded ones [2]. These facts suggest that two (or four)-electron transfer to the surface-adsorbed oxygen ( $\text{O}_2$ ), requiring more anodic potential of electrons in photocatalyst particles, happens in FB-BTO without any co-catalyst loadings, while similar two-electron transfer proceeds with platinized tungsten(VI) oxide [3]. In this study, light-intensity dependence of the rate of acetic-acid decomposition was studied to obtain kinetic evidence for the multielectron transfer.

FB-BTO, composed of particles of spherical assembly of BTO flakes, was prepared following the previous report [1,2]. As-prepared FB, its ball-milled samples (L and H) and their 773 K-calcined samples (500FB, 500L and 500H) were used for decomposition

of acetic acid in aerobic aqueous suspensions under monochromatic photoirradiation by (A) a diffraction grating-type illuminator (max. 10 mW) or (B) a 365-nm UV-LED (max. 320 mW).

It was found that order ( $n$ ) of light-intensity dependences at four wavelengths (irradiation A) calculated by assuming;  $r = a \times I^n$  ( $r$ : rate,  $a$ : constant and  $I$ : light intensity). Except for the samples L and H at 380 and 410 nm, BTO showed almost first-order light-intensity dependences at wavelengths between 320 and 410 nm. With the higher intensity irradiation (irradiation B), the order was decreased to ca. 0.5 order for FB and L at a folding point. As has been reported previously, photocatalytic acetic-acid decomposition proceeds through radical-chain mechanism with an alkyl peroxy radical as a chain carrier when titania was used as a photocatalyst, and the order of light-intensity dependence was ca. 0.5 [4]. The above-mentioned first-order light-intensity dependence for the most BTO samples can be interpreted by combination of second-order dependence for the accumulation of two electrons to reduce  $\text{O}_2$  and 0.5-order dependence owing to the radical-chain mechanism. Difference in folding points of plots between FB and L was observed; a folding point for FB was appreciably lower than that of L. One of the possible reasons for this difference is that the probability of the second-photon absorption by one photon-absorbed FB particle within its lifetime is higher than that of L particle owing to larger volume of FB particles [5].

## REFERENCES

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