Kinetic analyses of multielectron water oxidation and oxygen reduction in heterogeneous photocatalysis by metal oxide particles

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Abstract: Multielectron transfer, e.g., water oxidation in water splitting or oxygen reduction in organics decomposition, occurs in heterogeneous photocatalyses, however, the mechanism has been discussed only from the viewpoint of thermodynamics, i.e., standard electrode potential and band structure of a given photocatalyst. In this study, light-intensity dependences of rate of photocatalytic water oxidation and oxygen reduction were studied to support multielectron transfer mechanism based on kinetic models using commercial titania and laboratory-made bismuth tungstate powders, respectively, under high-intensity 365-nm UV-LED photoirradiation. The results suggest that two-electron transfer by accumulation of photoexcited electrons/positive holes mainly occurs in both photocatalytic reactions.

Keywords: Heterogeneous photocatalysis, Light-intensity dependence, Multielectron transfer.

1. Introduction

For heterogeneous photocatalysis, it is well known that photocatalytic water oxidation into oxygen and oxygen reduction in organics decomposition are induced by particulate photocatalysts. These reactions have been presumed to proceed through a four-electron (hole) process, and therefore it is expected that reaction rate and the efficiency depend on irradiated light intensity and particle size of a photocatalyst, which influence the number of photons absorbed by one photocatalyst particle. In order to improve the reaction efficiency, many researchers have worked on the reaction of electron-hole pairs such as enhancing charge separation and decreasing recombination, but photoabsorption has hardly been discussed so far. In this study, we analyzed light-intensity dependences (LIDs) and particle–size dependences of reaction rate for photocatalytic water oxidation and oxygen reduction under high light-intensity UV-LED irradiation to clarify the correlation between reaction rate and photoabsorption.

2. Experimental

For water oxidation, a 30-mg portion of commercial titania was suspended in deaerated aqueous 0.05 mol-L^{-1} sodium iodate (pH 10) or iron(III) chloride (pH ca. 2) solution (3.0 mL). For oxygen reduction, laboratory-made bismuth tungstate (BWO) powders[1-3] (30 mg) were suspended in 5.0vol% aqueous solution (3.0 mL) of acetic acid. Photoirradiation was performed using highly intense 365-nm UV-LEDs (NS Lighting ULEDN-101) and the maximum power was ca. 340 mW, which is more than one-order of magnitude higher than those of UV light from ordinary mercury or xenon arc lamps. Those reactions were evaluated by analyzing liberation of O_2 and CO_2, respectively, by gas chromatography.

3. Results and discussion

Figure 1(a) shows double-logarithmic plots of LID of reaction rate with small-size anatase titania as a photocatalyst using iodate ion as an electron acceptor. In the relatively lower intensity region, second (< 100 mW) and first-order (< 280 mW) dependences were observed as was also seen in the reactions with small-size rutile titania even in the cases in which both iron(III) or iodate ions were used as electron acceptors. These dependences are attributable to two-electron process and the first-order dependence at the middle-intensity region might be because the two-photon absorption by one photocatalyst particle is guaranteed due to higher light intensity. Such LID-order switching could reasonably be explained using a kinetic model in which the probability of multiple-electron (positive holes) accumulation in each particle governs the overall rates. On the other hand, at the further higher intensity (> ca. 280 mW), fourth-order dependence appeared. Since the electrode potential of four-electron reaction (+1.23 V) is lower than two-electron reaction (+1.77 V), it was presumed that the probability of four positive-hole accumulation in one photocatalyst particle under high-intensity irradiation became appreciable to induce four-electron transfer to water[4].

Similar bimodal LID-order switching, first and 0.5th in the lower and higher intensities, respectively, was observed in the case of photocatalytic decomposition of acetic acid using BWO as a photocatalyst as shown in Fig. 1(b). The particle size of BWO dominates the probability of accumulation of two excited electrons in one particle, to result in regulating overall photocatalytic reaction rate, and those LIDs could be reasonably explained by a kinetic model derived from radical chain reaction with peroxy radicals as a chain carrier and assumption that oxygen reduction occurs only when two electrons (and possibly four-electron at the highest intensity region) are accumulated in one photocatalyst particle. In addition, the threshold intensity between first and 0.5th-order LIDs (in 0.5th-order LID area, accumulation of the two electrons is guaranteed due to the higher light intensity) was appreciably lower than that for wet-milled-BWO, suggesting that oxygen reduction by BWO is two electron transfer reaction under the ordinary continuous-light-irradiation conditions and that the effect of particle size on the photocatalytic reaction rate is related to the probability that multiple electrons (holes) are generated in one particle[5].

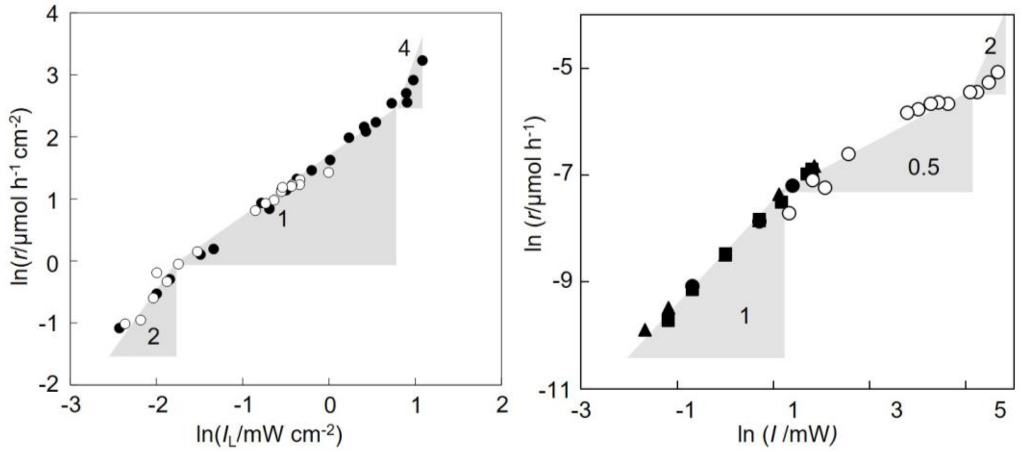

Figure 1. LIDs of reaction rates using (a) small anatase titania and iodate ion for water oxidation and (b) bismuth tungstate for oxygen reduction.

4. Conclusions

The LIDs of water oxidation and oxygen reduction using titania and bismuth tungstate particles, respectively, under intense UV-LED irradiation were multimodal; the LID changed from second to first order, and then fourth order for water oxidation and first to 0.5th and second for oxygen reduction. The kinetic analyses based on LID studies using high-intensity UV-LED might be unique and effective method exploring the intrinsic mechanism of heterogeneous photocatalysis. In addition, effective particle size of photocatalyst is important to enhance photocatalytic activity, especially for photocatalytic systems in which multielectron/positive hole transfer is included, resulting in probability of multielectron/positive holes accumulation in each particle.

References

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