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Author(s)	Torimoto, Tsukasa; Aburakawa, Yousuke; Kawahara, Yoichiro et al.
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Light Intensity Dependence of the Action Spectra of Photocatalytic Reactions with

Anatase Titanium (IV) Oxide

Tsukasa Torimoto,^{ab} Yousuke Aburakawa,^b Yoichiro Kawahara,^b Shigeru Ikeda,^{ab} and

Bunsho Ohtani^{ab*}

^aCatalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan.

^bGraduate School of Environmental Earth Science, Hokkaido University, Sapporo

060-0810, Japan

Corresponding Address:

Prof. Bunsho Ohtani

Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan.

Phone: +81-11-706-9132

Fax: +81-11-706-9133

e-mail: ohtani@cat.hokudai.ac.jp

Abstract

Light intensity dependence of action spectra of photocatalytic reactions was investigated using anatase single-phase titanium (IV) oxide powders as photocatalysts. The action spectra normalized at 350 nm were not changed in methanol dehydrogenation with the range of intensities of ca. 0.1 - 10 mW cm⁻², while those for acetic acid decomposition were red-shifted with increase in light intensity. The apparent quantum yield of the former was almost independent of the irradiation intensity, but that of the latter was declined with increase in light intensity, the degree being considerably enhanced with the irradiation at shorter wavelength if the light intensity was higher than 2 mW cm⁻². These can be explained by the difference in the utilization efficiency of photogenerated charge carriers.

Introduction

Analysis of action spectra, plots of photochemical reaction rate or yield per unit number of photons as a function of monochromatic light wavelength, is a useful method for identifying photoactive species, such as photoinitiators, photosensitizers and photocatalysts, which induce photochemical reactions. Action spectrum analysis has also been applied to photocatalyses by particles of a semiconductor such as titanium (IV) oxide (TiO_2) to prove that the semiconductor particles used could actually photocatalyze, for example, hydrogen evolution [1,2], oxidative decomposition of organic compounds [3-6], and photocurrent generation [7-9], by checking that their action spectra are similar to absorption or reflectance spectra of the semiconductor particles. Since both absorption and action spectra of a semiconductor photocatalyst are rather structureless in many cases, we can discuss their onset wavelength corresponding to the band gap of the semiconductor (ca. 390-410 nm for TiO_2) and then determine whether a certain photoreaction is catalyzed by the photocatalyst. We have recently reported action spectra analyses of photocatalytic reactions driven by anatase-rutile mixed TiO_2 powders [10]. It was revealed for the first time that the crystalline phase of relatively high photocatalytic activity could be identified by comparison of action spectra with diffuse reflectance spectra of the TiO_2 samples. The

observed active crystalline phase in TiO₂ powder differed depending on the kind of photocatalytic reaction; although the profile of an action spectrum of a photocatalytic reaction almost coincided with the absorption spectrum when anatase and rutile phases showed comparable photocatalytic activities (methanol dehydrogenation under deaerated conditions), the action spectrum profile of mixed TiO₂ powders resembled the absorption spectrum of pure anatase or rutile when the anatase phase or rutile phase was almost solely responsible for the photocatalytic activity (acetic acid decomposition or silver metal deposition, respectively). These results clearly show that an action spectrum is a product of spectra of photoabsorption and photocatalytic reaction efficiency utilizing photoexcited electrons (e⁻) and positive holes (h⁺) generated by photoabsorption. For example, when the anatase phase in the mixture shows relatively high photocatalytic activity, the reaction efficiency of the rutile phase becomes negligible in the whole range of wavelengths and the overall action spectrum therefore reflects the behavior of the anatase phase.

On the basis of these results and considerations, we can expect that for a certain photocatalytic reaction under favorable conditions the action spectrum may give us information on the wavelength dependence of the reaction efficiency of e⁻ and h⁺ as a difference in the profile from that of the photoabsorption spectrum. In this study, we

investigated the action spectra of photocatalytic methanol dehydrogenation (H_2 evolution) under deaerated conditions and of acetic acid decomposition (CO_2 evolution) under aerated conditions with irradiations at various average light intensities. To prevent the influence of a multiple crystalline phase of various photocatalytic activities, TiO_2 samples containing only anatase crystallites were used. The choice of anatase, not rutile, was based on the fact that anatase shows relatively high activity for reactions under aerated conditions similar to those of the practical application of TiO_2 photocatalytic reactions to decontamination of organic compounds.

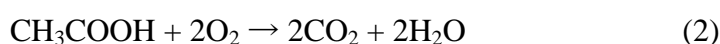
Experimental

A TiO_2 powder purchased from Merck (BET surface area: $13 \text{ m}^2\text{g}^{-1}$) and a reference catalyst (JRC TIO-2, $18 \text{ m}^2\text{g}^{-1}$) supplied by the Catalysis Society of Japan were used throughout this study. The purity of anatase was confirmed by checking that there were no detectable XRD peaks assigned to rutile. They were platinized before being used in methanol dehydrogenation (reaction (a)); TiO_2 (50 mg) suspended in an aqueous solution (5.0 cm^3) containing methanol (50 vol%) and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was irradiated with a high-pressure mercury lamp ($\lambda > 300 \text{ nm}$) and this was followed by washing with water several times and drying to achieve 2-wt%

loading of platinum (Pt). Each photocatalyst (50 mg) was suspended in an aqueous solution (5.0 cm³) containing methanol (50 vol%; reaction (a)), or acetic acid (5.0 vol%; reaction (b)) and was irradiated under (a) Ar or (b) air with vigorous magnetic stirring (at ca. 1000 rpm). Action spectra were measured with monochromatic light irradiation in the wavelength range from 290 to 440 nm using a diffraction grating-type illuminator (JASCO, CRM-FD) equipped with a 300 W xenon lamp (Hamamatsu Photonics, C2578-02). The light intensity at each wavelength was adjusted by stainless-steel mesh filters. Since the monochromatic light had different intensities (within ca. 30%) depending on wavelength, the average intensity is shown for convenience in each set of irradiations. Full width at half-maximum intensity (FWHM) of monochromatic light was ca. 17 nm, irrespective of the wavelength.

Results and discussion

Previous studies have shown that the stoichiometries of predominant reactions occurring in reactions (a) and (b) are represented by eqs. 1 and 2, respectively [10].



Based on the assumption, for convenience, that equations (1) and (2) require 2 and 8

pairs of e^- and h^+ , respectively, the apparent quantum yield (Φ_{app}) was calculated as the ratio of the rate of e^- (h^+) consumption to the flux of incident photons.

Figure 1 shows the action spectra of the photocatalytic reactions of (a) and (b), normalized to Φ_{app} at 350 nm, at several light intensities of ca. 0.1–10 $mW\ cm^{-2}$ using Merck TiO_2 as a photocatalyst. Similar action spectra were obtained when TIO-2 was used as a photocatalyst. For reaction (a), the spectral shape was almost the same in spite of a considerable difference (ca. 100 times) in irradiation intensity. The onset wavelength were slightly (ca. 15 nm) red-shifted compared with that of the diffuse reflectance spectrum, probably due to the relatively large FWHM of monochromatic light for the reaction compared with that for diffuse reflectance measurement, as reported in our previous paper [10]; since photoabsorption by TiO_2 is always larger in the shorter wavelength (left) side than in the longer wavelength (right) side in a given wavelength range of monochromatic light, the action spectrum may be shifted to a longer wavelength.

On the other hand, the action spectra of reaction (b) were red-shifted with increase in intensity, and the onset wavelength at intensity of 7 $mW\ cm^{-2}$ was ca. 40 nm red-shifted compared with that of reaction (a) with a similar light intensity, when they were normalized at 350 nm. Since TiO_2 particles suspended in an aqueous solution

containing 5.0 vol% acetic acid could not give any considerable changes in diffuse reflectance spectra from that of TiO₂ particles in the powder form, we can rule out the possibility that the photoexcitation of an absorption band produced by the interaction between acetic acid and TiO₂ surface causes the difference in action spectra between reaction (a) and (b).

Figure 2 shows the dependence of Φ_{app} of photocatalytic reactions with use of Merck TiO₂ on the light intensity of irradiation. The use of TIO-2 powders gave similar light intensity-dependent behavior of Φ_{app} (not shown). In the case of reaction (a), almost constant Φ_{app} was obtained at each wavelength of irradiation light, irrespective of the intensity. This fact indicated that the action spectra almost coincided with each other even if the absolute value of Φ_{app} was plotted against wavelength. In contrast, the changes in the irradiation intensity greatly influenced Φ_{app} in reaction (b), as shown in Fig. 2b. Φ_{app} decreased almost linearly in logarithmic scale with an increase in the irradiation intensity up to ca. 2 mW cm⁻², regardless of the wavelength of irradiation. The slope of linear parts of lines in this intensity region was ca. -0.5 for all the wavelengths. Further increase in the irradiation intensity caused steep attenuation of Φ_{app} with a slope of ca.2. The inflection points shifted to higher intensity side along with irradiation wavelength. This behavior resulted in the

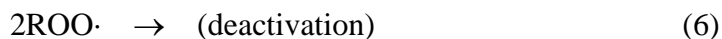
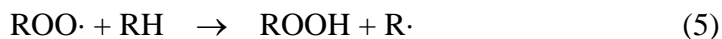
remarkable broadening of action spectra at higher intensity of irradiation light, and the red shift of action spectra normalized at 350 nm (Fig. 1b) was attributed to the largely decreased Φ_{app} at shorter wavelength, not to the increased Φ_{app} at longer wavelength.

As described in the introductory part of this paper, Φ_{app} is, in the first approximation, a product of efficiencies of photoabsorption and subsequent chemical reaction. The latter is called quantum efficiency and greatly affects the light intensity-dependent of Φ_{app} , because the former is expected to be constant independent of the intensity of irradiation light used in this study. Unfortunately, however, there is no technique for measuring the precise intensity of light absorbed by TiO_2 particles in suspension and therefore the chemical reaction efficiency can not be extracted from Φ_{app} obtained in this study. In the case of reaction (a), the observed constancy of Φ_{app} can be explained by the same light-intensity dependence of rates of chemical reaction and recombination of e^- and h^+ in the presumed reaction mechanism including them. Although at considerably high light intensity, for example, when an ultra-fast pulse laser was used, e^-h^+ recombination following second-order kinetics has been reported [11], at a low intensity of light from continuous light sources, mutual recombination obeying first-order kinetics might be a predominant process. Consequently, when it is also presumed that the rates of chemical reactions caused by e^- and h^+ are proportional to the

concentration of e^-h^+ pairs, that is, they follow the first-order kinetics, chemical reaction efficiencies must be independent of the light intensity, resulting in the constant Φ_{app} .

On the contrary, the simple discussion about the first-order kinetics in the reactions, in which e^- and h^+ participated, could not give any reasonable explanation for the results in reaction (b). Many papers on the mechanisms of photocatalytic decomposition of organic compounds have been published and the role of reaction intermediates has been discussed in detail, but even details of the mechanism of the initial step of photocatalytic oxidation, e.g., whether a hydroxyl radical ($\cdot OH$) (or h^+) participates or not, are still ambiguous [12-14]. However, at least in the presence of molecular oxygen (O_2), i.e., under aerated conditions, a radical chain mechanism including a peroxy radical ($ROO\cdot$) can be postulated [12,15,16]; a radical, $R\cdot$, is produced from the reactant, RH , by oxidation by h^+ with proton release or hydrogen abstraction by $\cdot OH$ and gives $ROO\cdot$, which abstracts hydrogen from RH to produce $R\cdot$ again, by the reaction with O_2 . The deactivation of $ROO\cdot$ occurs through bimolecular radical coupling processes. These are represented in eqs. 3 – 7.





This mechanism can produce a multiple number of $\text{ROO}\cdot$, leading to spontaneous formation of the final oxidation product from one $\text{R}\cdot$ (h^+), and the number is called “chain length”. Actually, it has already been claimed that the quantum efficiency of the acetaldehyde decomposition exceeds unity due to the radical chain mechanism [17]. In this study, the inclusion of radical chain mechanism was also implied in the reaction (b) from the value of Φ_{app} at 290 nm, ca. 1.2, with the irradiation intensity of 0.06 mW cm^{-2} .

One possible reason for the decreased Φ_{app} at higher excitation density is the limitation of the supply of O_2 from the gas phase of the reaction mixture, which can cause the diminution of $\text{ROO}\cdot$ in the reaction of eq. 4, but this probability seems unlikely because almost the same Φ_{app} was observed when O_2 had been charged instead of air in the reaction mixture. Another possible reason is the shortening of chain length due to deactivation processes. The concentration of intermediate radical species,

such as $R\cdot$ and $ROO\cdot$, becomes large at higher irradiation intensity. This situation also accelerates their deactivation processes (eqs. 6 and 7), and then the efficiency of h^+ utilization declined with an increase in the irradiation intensity, resulting in the decrease in Φ_{app} . Recently, Fujishima and co-workers have reported that the quantum yield in the photodecomposition of acetaldehyde and 2-propanol increased with decrease in irradiation intensity and explained the phenomena by the deactivation of radical species formed during photodecomposition processes [17,18]. Furthermore, since the photoabsorption coefficient of TiO_2 increases with decrease in wavelength, the irradiation at shorter wavelength induces higher density of photoexcitation. These also cause the acceleration of the deactivation of intermediate radical species as in the case in which light intensity at a fixed wavelength is enhanced, resulting in the shift of inflection point of lines in Fig. 2 to the lower intensity side along with the decrease in the irradiation wavelength.

Conclusion

This study demonstrated for the first time that the action spectra of anatase single-phase TiO_2 depended both on the kind of photocatalytic reaction and on the intensity of irradiation. The observed behavior could be interpreted by the dependence

of reaction rate on excitation density. Action spectra of photocatalytic reactions have been discussed so far mainly in relation to absorption properties of photocatalysts, and little attention has been paid to the influence of the reaction efficiency depending on the irradiation wavelength. The present study revealed that action spectrum analyses enable us to discuss the reaction mechanism that is related to the concentration of intermediate species in the actual time domain of a chemical reaction.

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Figure Captions

Figure 1 Action spectra of photocatalytic reactions of (a) methanol dehydrogenation and (b) acetic acid decomposition. Average light intensities of irradiation were 7.5 (circles), 1.4 (triangles), and 0.10 (squares) mW cm^{-2} for methanol dehydrogenation and 19 (circles), 7.0 (triangles), and 0.10 (squares) mW cm^{-2} for acetic acid decomposition. Merck TiO_2 powder was used as a photocatalyst. The dotted lines represent diffuse reflectance spectra of the photocatalyst.

Figure 2 Dependence of Φ_{app} of (a) methanol dehydrogenation and (b) acetic acid decomposition on the intensity of irradiation. The wavelength of irradiation light were 290 (open circles), 350 (solid circles), 380 (open squares), and 395 nm (solid triangles). Merck powders were used as photocatalysts.

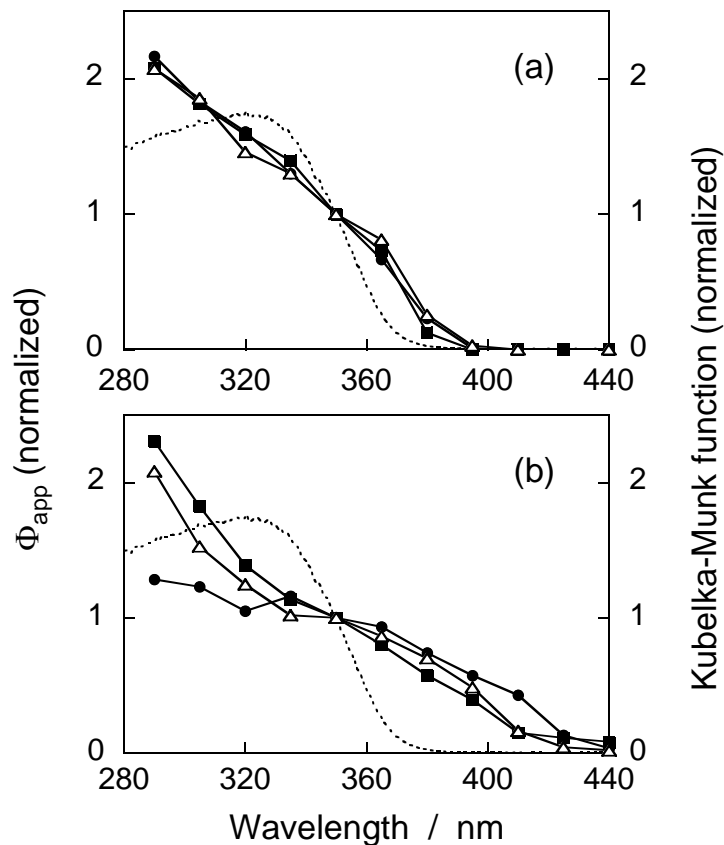


Figure 1 Action spectra of photocatalytic reactions of (a) and (b). Average light intensities of irradiation were 7.5 (circles), 1.4 (triangles), and 0.10 (squares) mW cm⁻² for methanol dehydrogenation and 19 (circles), 7.0 (triangles), and 0.10 (squares) mW cm⁻² for acetic acid decomposition. Merck TiO₂ powder was used as a photocatalyst. The dotted lines represent diffuse reflectance spectra of the photocatalyst.

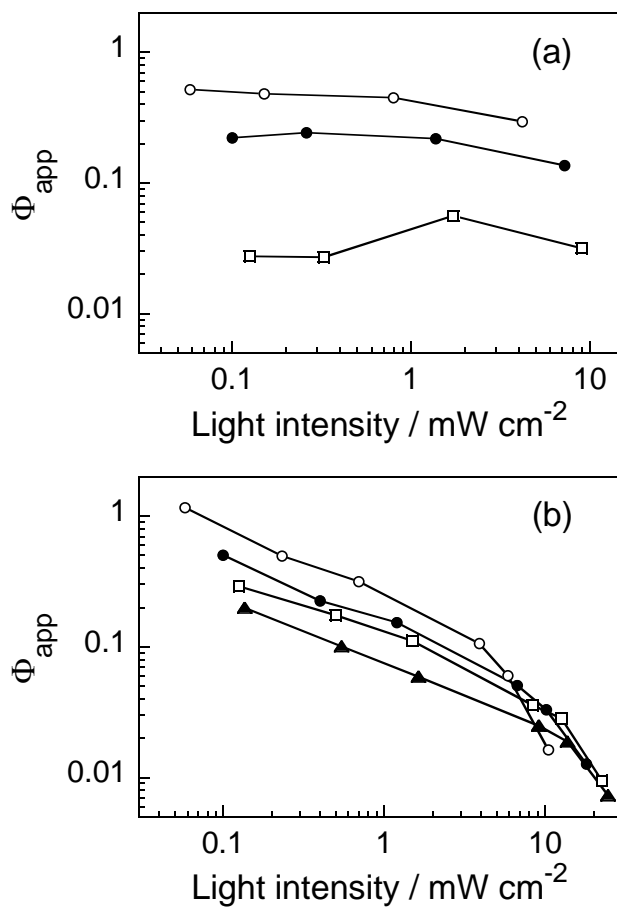


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