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Revisiting the Fundamental Physical Chemistry in Heterogeneous Photocatalysis: Its Thermodynamics and Kinetics

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Although the history of photocatalysis research is not so long, many researchers have studied photocatalysis and a large number of papers on photocatalysis have been published. The objectives of this review paper are to revisit the fundamentals of photocatalysis, especially its thermodynamics and kinetics, which have not been reexamined in recent studies, to clarify the problems, if any, that prevent developments in the field of photocatalysis, and to present insights for future progress.

What we know and we don't know about photocatalysis: an introduction

Heterogeneous photocatalysis has been believed, at least in early studies in 1980's and 1990's, to be a dream technology for solving energy and/or environmental problems that we are facing. However, photolysis of water into hydrogen, a fuel, and oxygen¹ has not yet been realized as an industrial process, and photocatalysts working under visible-light irradiation with activity higher than that of titanium(IV) oxide (titania) powders under ultraviolet-light irradiation² have not yet been developed despite extensive studies for more than a quarter of a century. The principle, a basic mechanism of heterogeneous photocatalysis, seems not to have changed, reading original and review papers on heterogeneous photocatalysis. Then, why have we not succeeded in practical applications of photocatalysis? Are there any hidden secrets preventing progress in photocatalysis studies? This review paper aims at clarifying what we know, what we don't know and what we should know for heterogeneous photocatalysis in a strict scientific sense and at suggesting insights for future progress. The author thanks the readers for their understanding that some of the concepts discussed in this paper have already been shown in his recent review papers^{3,4} and book sections.^{5,6}

Heterogeneous photocatalysis is categorized as physical chemistry and there are two fundamental concepts in physical chemistry, thermodynamics and kinetics. The thermodynamics of heterogeneous photocatalysis is first discussed, followed by discussion on its kinetics.

Thermodynamics

Thermodynamics predicts whether a chemical reaction proceeds or not by showing the equilibrium of the reaction. According to text books on thermodynamics (or text books on physical chemistry), a forward reaction proceeds when Gibbs energy change (ΔG) is negative and a reversed reaction proceeds when ΔG is positive. Then, how can we evaluate ΔG and predict the reaction equilibrium in photocatalysis?

Thermodynamic requirements for photocatalysis

The mechanism of heterogeneous photocatalysis⁷ is always explained with a band structure of electronic energy in photocatalysts, as Fig. 1 shows.

(Fig. 1)

An electron in a filled valence band (VB) is excited into a vacant conduction band (CB) state by a photon of energy greater than the energy of the gap between the VB and the CB, the band gap;⁸ CB bottom and VB top positions determine the ability of reduction and oxidation by a photoexcited electron (e^-) and a positive hole (h^+), since those charge carriers are to be thermally relaxed to the CB bottom and VB top, respectively, immediately after photoexcitation. It has been believed that the requisites for a photocatalytic reaction are: (1) redox potential, i.e., standard electrode potential, of a substrate to be reduced (P_{red}) is lower, i.e., more anodic, than the CB bottom and (2) redox potential of a substrate to be oxidized (P_{ox}) is higher, i.e., more cathodic, than the VB top. Since the overall Gibbs energy change, ΔG , corresponds to the difference between P_{red} and P_{ox} , ΔG is positive when P_{red} is higher, i.e., more cathodic, than P_{ox} , and ΔG is negative when P_{red} is lower, i.e., more anodic, than P_{ox} , and thereby positive- ΔG reactions, as well as negative- ΔG reactions, can be driven by photocatalysis.

Then, how are photocatalytic reactions regulated by their overall ΔG ? Actually, photocatalytic reactions, different from ordinary thermal catalytic reactions, can be driven in the opposite direction than predicted based on their overall ΔG , using light. since light energy is introduced into the reaction systems for photocatalytic reactions (and for photoreactions). The above-mentioned requisites relating to redox potentials and band positions mean that partial ΔG in the steps of reduction and oxidation by e^- and h^+ , respectively, must be negative. Thus, as is also seen in ordinary chemical reactions, photocatalytic reactions are governed by partial ΔG s (ΔG_e and ΔG_h in Fig. 1). This seems to be well understood by researchers in the field of photocatalysis. However, a plausible misunderstanding is that those band-position conditions are "sufficient conditions" but not two of the "necessary conditions". There should be, at least, another hidden necessary condition for photocatalysis, as discussed in a following section.

Band position

On the basis of the above-mentioned considerations, estimation of positions of the CB bottom and the VB top of photocatalysts is very important, but how can we estimate these positions? One way to estimate band positions has been electrochemical measurement for an electrode prepared with the material of a photocatalyst. For example, for titania photocatalysts, an electrode of a reduced single crystal of or sintered polycrystalline titania has been used for the measurement, and the CB bottom position is estimated from flat-band potential by checking potential-photocurrent curves or a Mott-Schottky plot.⁹ If the electrode is adequately prepared and treated to show an n-type semiconductor property (for titania), data might be obtained without arbitrariness, i.e., the same, or similar in a scientific sense, CB bottom position can be estimated by anyone. On the other hand, it seems that the position of the VB top is hard to be estimated directly, especially for particles, and thereby the VB-top position has been estimated from the CB-bottom position and the band gap since the difference between the CB bottom and VB top corresponds to the band gap. Then, how can we estimate band-gap energy of a photocatalyst? One possible method is to use a photoabsorption spectrum, i.e., so-called Tauc plot;¹⁰ the n th power of the product of Kubelka-Munk function ($F(R)$) and photon energy ($h\nu$) of diffuse-reflectance of a photocatalyst is plotted against wavelength. This Tauc plot seems to be often misunderstood: many reports have claimed that the transition mode, direct, indirect or others, of band-to-band excitation could be determined by comparison of plots with different n values.

(Fig. 2)

Although his paper has not been referred to frequently, Scaife reported the determination of band positions of a large number of simple and mixed metal oxides by electrochemical measurements.¹¹ Both flat-band potential (V_{fb}) and band gap (E_g) of more than forty simple or mixed-metal-oxide electrodes were measured by analysis of photocurrent–applied potential relations, without using Mott–Schottky plots of capacitance, and wavelength dependence of photocurrent, respectively. For the determination of band gaps, the author used the following equation:

$$\frac{h\nu \cdot J_v}{e\phi_\nu} = C(h\nu - E_g), \quad (1.1)$$

where h , ν , J_v , e , ϕ_ν , C , and E_g are Planck constant, vibration frequency, photocurrent by irradiation of light with vibration frequency ν , electronic charge, flux of photons of ν , a constant, and band gap, respectively, and a general relationship between them was shown as

$$V_{fb}(\text{SHE}) = 2.94 - E_g. \quad (1.2)$$

(Fig. 3)

The methods for band-position estimation employed by Scaife were different from generally accepted equations, Tauc plots, for direct and indirect band-gap semiconductors. It seems reasonable not to use Tauc plots, since there was no way to know whether a given metal oxide was a direct or indirect semiconductor; Tauc plots can predict band-gap energy only when transition mode, direct, indirect or others, is assumed. The present author also pointed out in a recent review⁴ that band-gap determination by plots of photoabsorption or related parameters assuming direct or indirect transitions has an essential problem due to a misunderstanding of the formula for direct and indirect transitions; actually both plots have linear parts giving different band gap values, i.e., it is rather difficult to determine the mode of transition of a given sample by comparison of the plots, as shown in Fig. 2. This had already been pointed out by Scaife more than thirty years ago, but nobody, as far as the present author knows, has considered this problem, and comparison of plots for direct and indirect transitions is still being made.

While plots for some of metal oxides with partly filled d-levels deviated from the line,¹² all metal oxides without partly filled d-levels obeyed the relationship of eq. 1.2. The equation suggested that the position of the VB top is constant regardless of the kind of metal in the metal oxides. This seems reasonable assuming that the VB of metal oxides predominantly consists of O 2p orbitals in metal oxides, as has been recognized in the past decade for interpretation in "band engineering" for visible light-sensitive photocatalysts. However, Scaife's paper has rarely been regarded as an original paper and has not been cited frequently in review articles on photocatalysis. This is possibly due to a preceding paper discussing the band positions of various semiconductors by Gleria and Memming, who reported the band positions of several semiconductors not limited to metal oxides,¹³ and later Watanabe et al. reported those in addition to some metal oxides in their review article written in Japanese.¹⁴ It is interesting to find inconsistency with Scaife's estimation, i.e., band positions of metal oxides in these papers were different. Thus, for the determination of band positions, a significant property of a given photocatalyst, there seems to be no consensus. This problem will be discussed again in another opportunity.¹⁵

Honda-Fujishima effect

It seems that the most frequently cited paper in the field of photocatalysis is a paper by Fujishima and Honda published in 1972 in *Nature*¹⁶ (6,903 times as of August 11, 2013¹⁷), and this paper has been called a paper on the "Honda–Fujishima effect" in Japan. Although the seminal Fujishima and Honda paper was strictly photoelectrochemical, it has been cited by the photocatalysis community as an original paper on titania photocatalysis. For this reason, and the fact that it was one of the earliest published report of light-driven titania photochemistry, the author presents a detailed account of this landmark discovery. Before starting discussion of this paper, it should be

pointed out that no descriptions related to photocatalysis, such as "photocatalysis", "photocatalyst", or "photocatalytic" and no description of photocatalysis by titania appeared in this paper. This is reasonable considering the title of this paper, "Electrochemical Photolysis of Water at a Semiconductor Electrode". These facts suggest that this paper cannot be an origin of photocatalysis in a bibliographic sense, though this paper did indeed promote photocatalysis studies and, actually, the author started his research career in the "boom" of photocatalytic studies initiated by this paper. The problem is not the fact of such inappropriate citations but that few readers have noticed a suggestion in the paper.

This paper, consisting of only about one page, had, unfortunately, some ambiguous descriptions, especially in the experimental section. The caption for Fig. 1 in the paper, for example, showing current–potential curves of a single-crystalline titania anode under photoirradiation did not show pH and content of the electrolyte solution. By comparison with a similar current–potential curve reported by the same authors three years before publication of this paper,¹⁸ the electrolyte solution was probably aqueous potassium chloride buffered with acetate/acetic acid (acetate buffer) at pH 4.7.¹⁹ Under these conditions, anodic photocurrent was observed at an electrode potential more anodic than ca. -0.5 V versus SCE (similar to Fig. 4(f)). Although there was also no description of the current–potential curve of a platinum cathode in the dark, electrode potential for hydrogen evolution at the cathode had been reported to be ca. -1 V versus SCE at pH 4.7 in the previously published paper.¹⁸ This cathode potential was more cathodic than the onset potential, ca. -0.5 V versus SCE, for oxygen evolution at the photoirradiated titania anode and this suggested that short circuiting of the electrodes does not give any current between them, i.e., electrochemical bias of at least 0.5 V is necessary to decompose water into hydrogen and oxygen at the titania photoanode and the platinum cathode, respectively, when those two electrodes are immersed in an electrolyte solution.

The composition of electrolytes in the experiment for which results are shown in Fig. 2 of the paper was also unclear. Photoirradiated titania and dark platinum electrodes were wired directly to each other with a resistance, and photocurrent from platinum to titania was detected without electrochemical bias between the electrodes. However, numbers 1–5 were presented in the figure without related descriptions.²⁰ Again, there was no description of the electrolyte solution(s) in this electrochemical cell. The photoelectrochemical experiments used in the Honda and Fujishima paper were reproduced and checked by Nozik²¹ and Wrighton and co-workers.²² They reported based on the detailed analyses that pH gradient between anode and cathode compartments was necessary to observe oxygen and hydrogen evolution from a short-circuited single-crystal titania anode and a platinum cathode, respectively. Therefore it seemed that bias potential had been applied chemically in the Fujishima and Honda's experiment, though no electrochemical potential bias was applied using an outer circuit.

Thus, two examples of water photolysis were suggested in the paper, but both of those seemed to require electrochemical or chemical "bias" for the system including a titania photoanode and a platinum cathode as has been already pointed out in 1975.^{21,22} The bias application creates the depletion layer with potential slope enough steep to separate $e^- - h^+$.²³ This might be very important to understand heterogeneous photocatalysis as discussed in the next section. This paper could be an origin of research work on photocatalysis by titania particles, especially for photoinduced cleavage of water into hydrogen and oxygen, if no bias, even chemical bias, was being applied to the electrochemical system of short-circuited titania.

Photoelectrochemistry and photocatalysis

In the 1980's, photocatalysts such as platinum-loaded titania particles were often called miniature photoelectrochemical cells composed of a titania photoanode short-circuited with a platinum cathode;²⁴ e^- migrates to platinum deposits to reduce protons (or water) on their surface and positive holes oxidize substrates adsorbed on the titania surface. However, as mentioned above,

bias, electrochemical or chemical, had been required for the decomposition of water into hydrogen and oxygen at least for a short-circuited platinum-titania photoelectrochemical cell. One of the possible reasons for negligible simultaneous production of hydrogen and oxygen on a photoirradiated platinum-loaded titania photocatalyst is lack of bias potential between a titania anode and a platinum cathode.

Why is bias application necessary for the photoelectrochemical cells? Since, for example, the CB-bottom position of titania seems to be almost the same as the standard hydrogen electrode potential (SHE) and the VB-top position is far more anodic than the standard electrode potential of oxygen/water (+1.23 V vs SHE), h^+ in titania can oxidize water without applying bias potential. Since electrons in a donor level near the surface for an n-type semiconductor (n-SC in Fig. 4(a) and (b)) like reduced single-crystal titania flow out to make a depletion layer inside the electrode, band levels shift slightly in the anodic direction. This shift causes the shift of on-set potential for photoanodic current from the rest potential, i.e., bias potential, at least compensating the band-level shift (Schottky-type barrier²⁵) in the depletion layer, is required for the photoelectrochemical reaction. It is probable that the potential slope in the semiconductor electrode due to the formation of a depletion layer and/or the application of bias potential enables the separation of e^- and h^+ , charge separation, prohibiting their recombination. Thus, redox reactions by e^- and h^+ proceed only when these charge carriers are separated from each other, escaping from their mutual recombination. A suggestion in the paper by Fujishima and Honda¹⁶ is that the charge separation is one of the requisites for photoinduced redox reactions by semiconducting materials, i.e., photocatalysis, in addition to the requisites for band positions as described in the preceding section

(Fig. 4)

On the other hand, for photocatalysts, charge separation by the depletion layer is scarcely expected, because donor density of particulate photocatalysts is low, potential slope in the layer should be negligible. Furthermore, it is very challenging to apply bias potential, i.e., to introduce two contacting phase potentials to particles using solution redox couples. Why do photocatalytic reactions actually proceed? One of the reasons is irreversible processes by e^- and/or h^+ . When one of the charge carriers is captured by a substrate molecule irreversibly, the other charge carrier left in the photocatalyst particle can react since there are no counter carriers. In studies for development of photocatalysts for water splitting, test reactions for hydrogen and oxygen evolutions used, respectively, sacrificial electron donors and acceptors, which capture h^+ and e^- , irreversibly. The fact that most photocatalysts with activities for hydrogen and oxygen evolutions in the presence of an electron donor and an electron acceptor, respectively, cannot work for water splitting in the absence of sacrificial agents suggests the importance of the charge separation as a necessary condition. We should be reminded that, even at about forty years after the publication of Fujishima and Honda's paper, chemists in the field of photocatalysis have not overcome the bias problem to achieve efficient photocatalytic water splitting, especially under visible-light irradiation, except for few successful results by the groups of Domen, Kudo and Abe.¹

Particle anisotropy and built-in electric field

Then, what is a possible strategy for charge separation in photocatalytic reaction systems? The answer is building an electric field in photocatalyst particles, i.e., built-in electric field, and anisotropy of a photocatalyst particle is one of the possible solutions for building of an electric field in it.

It has often been reported that loading of a noble metal, such as platinum, enhances the photocatalytic activity of bare metal oxide or sulfide particles. While this enhancement may be mainly due to the promotion of hydrogen evolution or oxygen reduction on the noble-metal deposits, irreversible capture of e^- , if possible, might produce an electric field. It has often been claimed that deposition of metal or metal oxide separates sites for photoexcited electrons and positive holes

to induce charge separation, though it seems impossible to separate charge carriers in a particle only by surface sites without an electric field to overcome electrostatic attraction between e^- and h^+ .

Recently, liquid and gas-phase synthesis and high-level photocatalytic activities of faceted titania particles, e.g., decahedral²⁶ and octahedral^{26b,27} anatase particles, have been reported by several groups including ours. As has been discussed extensively, correlations of the physical and structural properties and the photocatalytic activities of photocatalysts is not straightforward, and it is rather difficult, in a strict scientific sense, to attribute higher-level photocatalytic activity, if observed, to the crystalline shape exposing specific facets. However, there is still a possibility that anisotropy of particle shape governs the photocatalytic activity and that a built-in electric field inside the particle induces the separation of charge carriers, e^- and h^+ .

Kinetics

When a given photocatalyst and reaction conditions satisfy thermodynamic requirements for photocatalysis, the photocatalytic reaction may proceed. Then, how fast does the reaction proceed? Rates of chemical reactions can be predicted by kinetics, according to text books on physical chemistry. We often encounter the situation of comparing photocatalysts with their "photocatalytic activity" by measuring photocatalytic reaction rate. Then, how can "photocatalytic activity" be evaluated? The kinetics of a photocatalytic reaction is discussed in this section.

Activation energy and rate-determining step for photocatalysis

In ordinary chemical reactions, rate of the reaction is proportional to the concentration of a substrate, and the proportional constant, i.e., a rate constant, is governed by activation energy, ΔE_a , barrier height in a path of the rate-determining step. It is also predicted theoretically that ΔE_a is proportional to overall Gibbs energy change (ΔG).²⁸ Since photocatalytic reactions proceed even when overall ΔG is positive as discussed in the preceding section, the rate of photocatalytic reactions may not be controlled by ΔE_a . Actually, reported ΔE_a values measured in a variety of photocatalytic reactions were around 10 kJ mol^{-1} , much smaller than those of ordinary chemical reactions, as has been discussed in a recent review.^{3,4} This is reasonable considering that the mechanism of photocatalytic reactions includes recombination of e^- and h^+ (e^-h^+ recombination) as well as their redox reactions, and even if e^-h^+ is assumed to be an activated state it is created by light energy but not thermal energy evaluated from the reaction temperature.

An Arrhenius plot, logarithm of a rate constant versus reciprocal temperature, gives "activation energy", but there is no guarantee that calculated activation energy reflects a "chemical" step. When a given reaction includes a rate-determining chemical step of the highest activation energy, the calculated activation energy corresponds to that of the rate-determining step, but even if a linear Arrhenius plot is obtained, it does not mean that the reaction system includes a rate-determining chemical step. In the field of photochemistry, activation energy and rate-determining step are rarely discussed because, generally speaking, photochemical reactions are not series reactions including a rate-determining chemical step and the observed relatively low activation energy therefore often corresponds to a physical step, e.g., diffusion of a substrate depending on the reaction temperature.⁴ Considering that photocatalysis is essentially a photochemical reaction, discussion of the rate-determining chemical step does not make sense.

Langmuir adsorption and first-order kinetics

In recent years, many papers have shown linear double-reciprocal plots of the rate of a photocatalytic reaction and concentrations of substrates in solution to interpret reaction kinetics, which was called the "Langmuir–Hinshelwood (L-H) mechanism",²⁹ in which the following equation was assumed.

$$r = \frac{kKC}{1+KC} \quad \text{or} \quad \frac{1}{r} = \frac{1}{kK} \times \frac{1}{C} + \frac{1}{k}, \quad (2.1 \text{ and } 2.2)$$

where r , k , K and C are rate, rate constant, Langmuir adsorption constant, and concentration of the substrate, respectively. The constant k , calculated as a reciprocal of an intercept of the plot for eq. 2.2 is not a so-called rate constant reflecting the reactivity of e^-h^+ . Considering that a part $KC/(1+KC)$ must be dimensionless, the unit of k should be the same as that of r , i.e., reaction rate. Thus, k is a limiting rate of the reaction at infinite C and is a product of N_s , saturation limit of Langmuirian adsorption, and a true rate constant k' . Therefore, the limiting rate k could be ideally proportional to specific surface area of a given photocatalyst, since the saturation limit of adsorption is a product of surface density of adsorption sites and specific surface area. However, such discussion has been negligible in the field of photocatalysis.

The above-mentioned so-called L–H mechanism has been used for discussion of the rate of photocatalytic reaction with various concentrations of a reaction substrate. On the other hand, "first-order kinetics" has often been used for discussion of time courses of photocatalytic reactions, and resultant (pseudo) first-order rate constants were compared for different kinds of photocatalyst. In general, the logarithm of the concentration of substrate (or product) or its equivalent is plotted against time of the reaction, i.e., photoirradiation, and the slope (absolute value) of a linear relation, if obtained, corresponds to a (pseudo) first-order rate constant. A number of papers on photocatalysis have shown that the substrate concentration dependence obeys the L–H mechanism showing the plot according to eq. 2.2 and that the time course obeys first-order kinetics showing the above-mentioned plot. However, it is impossible to satisfy both of those situations, except for the case where the substrate concentration is so low that the adsorption amount is almost proportional to the concentration in solution, i.e., Henry-type adsorption. In any case, discussion of first-order kinetics in photocatalysis seems strange considering that photocatalytic reaction rate does not depend on activation energy, as described in the previous section.

Steady-state approximation

Then, what kind of kinetics can interpret the photocatalytic reaction rate. Contrary to expectation, the original idea of photocatalytic reaction kinetics was reported in 1972, the year of publication of the above-discussed Fujishima and Honda's paper, by Fleischauer and coworkers.³⁰ The paper entitled "Quantum Yields of Silver Ion Reduction on Titanium Dioxide and Zinc Oxide Single Crystals" showed the kinetics of silver metal deposition on surfaces of titanium(IV) oxide (TiO_2) and zinc oxide (ZnO) single crystals. As far as the present author knows, this paper is the first report in which the effect of Langmuirian adsorption of a substrate on the rate (or quantum efficiency) of photocatalytic reaction by TiO_2 is discussed.

The rate of photoinduced silver metal deposition was analyzed using a Stern–Volmer plot, a popular method in the field of photochemistry; double-reciprocal plots of the (apparent) quantum efficiency for the deposition (Φ)³¹ against concentration of silver ion (Ag^+) in solutions (C_{Ag}) gave almost straight lines for both TiO_2 and ZnO crystals, as

$$\Phi = \frac{\Phi_{\text{lim}} C_{\text{Ag}}}{C_{\text{L}} + C_{\text{Ag}}}, \quad (3.1)$$

where Φ_{lim} , and C_{L} are constants. This equation is transformed to

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{lim}}} + \frac{C_{\text{L}}}{\Phi_{\text{lim}}} \times \frac{1}{C_{\text{Ag}}}, \quad (3.2)$$

enabling estimation of Φ_{lim} and C_{L} from the linear plot for both TiO_2 and ZnO samples. In the first approximation, the authors assumed a reaction mechanism in which electrons photoexcited by the

efficiency ϕ react with surface-adsorbed Ag^+ (with the surface concentration N_{Ag}) to give deposits with a rate constant k_3 , otherwise e^- is deactivated with a rate constant k_4 , as

$$\Phi = \frac{\phi k_3 N_{\text{Ag}}}{k_4 + k_3 N_{\text{Ag}}} \quad (3.3)$$

Interestingly, this equation can be derived by "steady-state (stationary-state) approximation", which is often successfully used for reactions by a short-lived active species such as the photoexcited state of a given material (e^- and h^+ in a photocatalyst), assuming a constant concentration of e^- that is produced by photoabsorption of a photocatalyst and consumed by the surface reaction and the recombination with positive holes. Then the authors applied a Langmuir adsorption isotherm to represent N_{Ag} using C_{Ag} . Although the authors did not show the details of derivation in their paper, the derivation would be reproduced as follows. First, N_{Ag} is represented using a total (saturated) density of surface adsorption of Ag^+ (N_s) and adsorption rate constant (K) as

$$N_{\text{Ag}} = \frac{N_s K C_{\text{Ag}}}{1 + K C_{\text{Ag}}} \quad (3.4)$$

Then N_{Ag} s in eq. 3.3 are substituted to give

$$\Phi = \frac{\phi \frac{k_3 N_s}{k_4 + k_3 N_s} C_{\text{Ag}}}{\frac{k_4}{K(k_4 + k_3 N_s)} + C_{\text{Ag}}} \quad (3.5)$$

Constants Φ_{lim} , and C_L in eq. 3.1 are determined by comparing eqs. 3.1 and 3.5,

$$\Phi_{\text{lim}} = \phi \frac{k_3 N_s}{k_4 + k_3 N_s} = \phi \left(1 - \frac{k_4}{k_4 + k_3 N_s} \right) \quad \text{and} \quad C_L = \frac{k_4}{K(k_4 + k_3 N_s)}, \quad (3.6 \text{ and } 3.7)$$

and K is represented as follows,

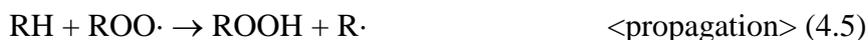
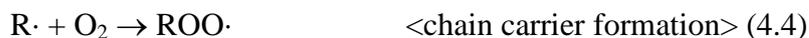
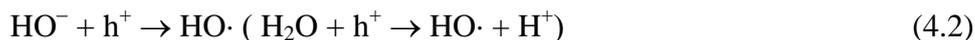
$$K = \frac{1 - \frac{\Phi_{\text{lim}}}{\phi}}{C_L} \quad (3.8)$$

Taking into account that apparent rate is a product of light flux and Φ and that both Φ_{lim} and C_L in eqs. 3.6 and 3.7, respectively, are independent of Ag^+ concentration in the solution, eq. 3.5 is equivalent to the so-called L-H kinetic equation in the preceding section (eq. 2.1). Thus, although this study used single crystals as a photocatalyst, the above-mentioned kinetic analysis had clearly reproduced the double-reciprocal linear relation between rate (quantum efficiency) and concentration of substrate in a solution, which are often observed in heterogeneous photocatalysis. This paper should be cited as an original paper of kinetic analysis based on Langmuirian adsorption of substrates in photocatalytic reactions.

Intrinsic quantum efficiency

A problem of the so-called L-H kinetic equation for photocatalytic reaction such as eq. 2.1 is that light flux, rate of photon incidence, does not appear clearly or it is also included in the apparent rate constant k . In other words, efficiency of photon utilization cannot be discussed, while the above-mentioned kinetic analysis based on steady-state approximation takes light flux into account.

For example, it has been claimed that a radical chain mechanism may enhance the photocatalytic decomposition of organic compounds (RH) in the presence of molecular oxygen (O_2), as



where radical species ($\text{R}\cdot$) are produced by direct oxidation by a positive hole (h^+) or hydrogen abstraction by hydroxyl radical ($\text{HO}\cdot$) liberated via eq. 4.2 followed by addition of O_2 to give peroxy radical ($\text{ROO}\cdot$) as a chain carrier. This relatively long-lived peroxy radical abstracts hydrogen in RH to produce another $\text{R}\cdot$ and then $\text{RO}\cdot$, and the resultant hydroperoxide (ROOH) is decomposed spontaneously. Chain length, number of $\text{ROO}\cdot$ liberated by initial $\text{R}\cdot$, is regulated by the rate ratio of steps 4.5 and 4.6, i.e., ratio of propagation and termination. It is expected that the higher is the concentration of $\text{ROO}\cdot$ by higher intensity photoirradiation, the faster is the termination to result in shorter chain length. However, the light-intensity dependence has rarely been discussed on the basis of the possible radical-chain mechanism.³²

What we observed as reaction rate may correspond to the rate of ROOH production leading to decomposition of a reaction substrate, and thereby "intrinsic quantum efficiency", efficiency of utilization of photogenerated active species, e.g., h^+ in the above-mentioned photocatalytic process, cannot be determined unless the rate of $\text{R}\cdot$ liberation via steps 4.1 and/or 4.3 is measured separately from that via step 4.5. In this sense, no reports on photocatalytic decomposition of organic compounds in the presence of O_2 have shown intrinsic photocatalytic activity, as fundamental knowledge of the reaction kinetics. A paper from the author's laboratory suggested that the intrinsic quantum efficiency for acetic-acid decomposition is very small and that the reaction is greatly enhanced by the above-mentioned radical chain mechanism, i.e., almost all e^- and h^+ recombine to induce no chemical reaction,³² as discussed in the next section.

Light intensity dependence

Since dependence of rate on temperature has often been measured in studies on catalysis, dependence of rate on light intensity has been measured, but the dependence seemed to be discussed from the standpoint of engineering to optimize the reaction conditions. Generally speaking, the reported light-intensity dependence was limited to reactions in the presence of O_2 and was approximately 0.5th order; the square-root of 2 times rate is observed when the light intensity is doubled. The reason for this dependence had been explained by the enhanced e^- - h^+ recombination due to their second-order recombination at a higher light intensity. This seemed reasonable assuming an appreciably long life time of e^- and h^+ waiting liberation of another pair in the same particle. However, in our study on light intensity dependence, such a reason for square-root dependence was excluded. While oxidative decomposition of acetic acid in an aerated aqueous solution by suspended anatase titania particles showed similar square-root dependence, i.e., apparent quantum efficiency was decreased with increase in light intensity of four monochromatic irradiation wavelengths, apparent quantum efficiency for methanol dehydrogenation by the same titania photocatalyst, loaded with platinum deposits, suspended in a deaerated aqueous solution was independent of light intensity, i.e., actual rate was proportional to the light intensity. Differences in these two reaction systems were presence/absence of O_2 and platinum.³² Based on the assumption that platinum deposits do not have an influence on the light intensity dependence, the difference in light intensity dependence between acetic-acid decomposition and methanol dehydrogenation is attributable to the mechanism of reaction in the presence of O_2 , not the enhanced e^- - h^+ recombination at a higher light intensity, as discussed in the preceding section.

Based on the assumption that the photocatalytic decomposition of acetic acid proceeds according to the mechanism including primary steps of eqs. 4.1, 4, 5 and 6, the apparent quantum efficiency (Φ_{app}) is derived as

$$\Phi_{\text{app}} = \phi\varphi + k_5 C \left(\frac{\phi\varphi}{k_6} \right)^{\frac{1}{2}} I^{-\frac{1}{2}}, \quad (5.1)$$

where ϕ , φ , k_5 , k_6 , C and I are intrinsic quantum efficiency, photoabsorption efficiency, rate constants for reactions eqs. 4.5 and 4.6, surface concentration of acetic acid on a photocatalyst and light intensity, respectively. Plots of Φ_{app} against $I^{-1/2}$ may be a straight line with a y-intersect as a product of ϕ and φ . However, actual plots shown in Fig. 5³³ with a negligible y-intersect suggest that the intrinsic quantum efficiency, i.e., efficiency of utilization of e^-h^+ , is very small and that appreciable overall apparent quantum efficiency is obtained by enhancement through the radical-chain mechanism. In other words, capture of e^- by O_2 on the surface of titania is not so efficient.

(Fig. 5)

Action spectrum as a proof for photocatalysis

A general understanding of the definition of "photocatalysis" is possibly "photoinduced reaction by absorption by a photocatalyst that is not changed by the reaction", and in this sense the photocatalyst needs not to be solid; organic compounds³⁴ and metal complexes can also be photocatalysts. In order to prove that a given reaction is this photocatalysis, two facts, i.e., experimental results, should be shown according to the definition. One is to show that only the "photocatalyst" absorbs light to induce the reaction and the other is to show that the "photocatalyst" does not change during and after the reaction, i.e., not a stoichiometric reaction. The concept of "turnover" has been commonly used to prove the latter; turnover number, molar ratio of a consumed substrate (or a liberated product) to a material as an assumed photocatalyst, has to exceed unity. On the other hand, proof for the former had been shown by control experiments; if the reaction occurs, by checking the reaction kinetics, only in the presence of a photocatalyst and a reaction substrate under photoirradiation, the reaction had (has) been believed to be "photocatalysis".

However, it has been shown that a certain non-photocatalytic reaction satisfies the control experiment: action-spectrum analysis of photoinduced reactions of methylene blue (MB) in an aqueous suspension of titania showed that MB adsorbed on the titania surface absorbs visible light, injects an electron to titania and is decomposed.³⁵ Since the electron injection from MB requires a solid material that adsorbs MB with an appropriate CB-bottom position, the above-mentioned control experiments suggest the MB reaction to be photocatalysis, i.e., the control experiments cannot exclude such non-photocatalytic dye-sensitized (dye-decomposition) reactions (Fig. 6). In other words, action-spectrum analysis is the only possible method to show what absorbs light to induce reactions.^{36,37} For these dye-sensitized reactions, kinetics must be different from the ordinary photocatalytic reactions by band-to-band excitation of photocatalysts, e.g., photoabsorption by MB on titania decreases along with MB decomposition.

(Fig. 6)

Conclusive remarks

It is surprising, at least for the author, that we know little about heterogeneous photocatalysis even though extensive studies have been carried out for more than forty years after the first-generation boom induced by the publication of a paper by Fujishima and Honda.¹⁶ What does this mean? There should be missing concepts, properties of photocatalysts or primary steps in photocatalysis that have not been noticed or understood but prevent progress of studies in the field of photocatalysis.

As an example of missing concepts, true interpretation of the excited state of particulate photocatalysts, which we believe to be formation of e^- and h^+ in the CB and VB of a photocatalyst, as well as their recombination, should be clarified. As an example of missing properties of photocatalysts, structural characterization of the recombination center in particles, which is believed to be a crystalline lattice defect,³⁸ is needed. An example of missing primary steps in photocatalysis is reduction of O_2 molecules adsorbed on the particle surfaces, the fate after reduction and the role of intermediate species in the mechanism.

The most important but unknown point must be e^-h^+ recombination. The only thing we know about the recombination in particulate photocatalysts is that it occurs to result in quantum efficiency smaller than 100%. As described above, we don't know where, when and how the recombination occurs. Since so-called photocatalytic activity is governed predominantly by the rate of recombination, as an intrinsic property, particulate materials with high-level photocatalytic activity can be designed only when the recombination in the materials is regulated, and we should focus on studying the recombination in photocatalysis, hopefully by collaboration with researchers in other fields. The author hopes that this review paper will help such progress in those studies.

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References and notes

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1. As recent reviews, introducing leading studies by the groups of Domen, Kudo and Abe, see: (a) R. Abe, *J. Photochem. Photobiol. C Photochem. Rev.*, 2010, **11**, 179–209. (b) K. Maeda, *J. Photochem. Photobiol. C Photochem. Rev.*, 2011, **12**, 237–268.
2. As a recent review, see: B. Ohtani, *Recent Pat. Eng.*, 2010, **4**, 149–154.
3. B. Ohtani, *Chem. Lett.*, 2008, **37**, 216–229.
4. B. Ohtani, *J. Photochem. Photobiol. C Photochem. Rev.*, 2010, **11**, 157–178.
5. B. Ohtani, *Solar Photocatalysis* (H. Suib ed.), Elsevier, Amsterdam, 2013, 121–144.
6. B. Ohtani, *Advances in Inorganic Chemistry* (R. van Eldik and G. Stochel eds.), Elsevier, Amsterdam, 2011, **63**, 395–430.
7. The word "heterogeneous" in the term "heterogeneous photocatalysis" means that the systems are heterogeneous, i.e., solid photocatalysts are in gas or liquid phases, i.e., "heterogeneous" indicates the reaction conditions. Therefore, the expression "heterogeneous photocatalyst" does not make sense.
8. The term "semiconductor photocatalysis" is also substituted for the term "heterogeneous photocatalysis". Since semiconductors are always solid, the term "semiconductor photocatalysis" indicates almost the same phenomenon. However, the electronic structure of photocatalysts shown in Fig. 1 is representative not only of semiconductors but also insulators. The author thinks it necessary to clarify how semiconducting properties, e.g., presence of donor/acceptor levels, of photocatalysts influence their photocatalytic activity.
9. For example: A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 1980.
10. Frequently cited references for "Tauc plot": (a) J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status Solidi*, 1966, **15** 627–637. (b) J. Tauc, *Optical Properties of Solids* (F. Abeles ed.), North-Holland (1972). (c) E. A. Davis and N. F. Mott, *Philos. Mag.*, 1970, **22** 903–922.

11. D. E. Scaife, *Solar Energy* 1980, **25**, 41–54.
12. Many researchers in the field of photocatalysis might examine the properties and photocatalytic activities of those exceptional mixed metal oxides, such as chromium niobate or chromium titanate, possessing relatively narrow band gaps and keeping a more cathodic CB-bottom position. However, unfortunately, those metal oxides seemed to be stable only at limited pH as was discussed in the paper.
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15. B. Ohtani, *Electrochemistry*, to be submitted.
16. A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38. This work was introduced in a Japanese newspaper as "Honda–Fujishima effect".
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18. A. Fujishima, K. Honda and S. Kikuchi, *Kogyo Kagaku Zasshi*, 1969, **72**, 108–113.
19. One of the authors, Professor Fujishima, showed almost the same potential-current curves in his account paper with a caption showing that an electrolyte solution contained potassium chloride at pH 4.7 buffered by acetate buffer: A. Fujishima, *Electrochemistry*, 2008, **76**, 84–87 (in Japanese).
20. Professor Fujishima recently told this mistake for lack of interpretation in this figure (ref. 19).
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23. Although systems containing a titania electrode require bias for water photolysis, strontium titanate (SrTiO₃; (a) and (b)) and potassium tantalate (KTaO₃; (c)) electrodes work even without electrochemical or chemical bias. This might be due to their higher CB-bottom levels to create depletion layer inside the semiconductor electrodes. (a) J. G. Mavroides, J. A. Kafalas and D. F. Kolesar, *Appl. Phys. Lett.*, 1976, **28**, 241–243. (b) M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Arahamso and D. S. Ginley, *J. Am. Chem. Soc.*, 1976, **98**, 2774–2779. (c) A. B. Ellis, S. W. Kaiser and M. S. Wrighton, *J. Phys. Chem.*, 1976, **80**, 1325–1328.
24. The connection between titania and platinum is believed to be ohmic, and no barrier is expected between them, as shown in Fig. 4(c) and (d).
25. Schottky barrier is defined as the potential barrier created between an n-SC and metal with a work function lower (more anodic) than the Fermi level of the n-SC. Similar barrier is also made when n-SC is immersed in an electrolyte solution.
26. For example, our papers: (a) F. Amano, O.-O. Prieto-Mahaney, Y. Terada, T. Yasumoto, T. Shibayama and B. Ohtani, *Chem. Mater.*, 2009, **21**, 2601–2603. (b) B. Ohtani, F. Amano, T. Yasumoto, O.-O. Prieto-Mahaney, S. Uchida, T. Shibayama and Y. Terada, *Top. Catal.*, 2010, **53**, 455–461. (c) N. Sugishita, Y. Kuroda and B. Ohtani, *Catal. Today*, 2011, **164**, 391–394. Papers from the other groups: (d) H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng and G. Q. Lu, *Nature*, 2008, **453**, 638–642. (e) V. M. Menéndez-Flores, M. Nakamura, T. Kida, Z. Jin, N. Murakami and T. Ohno, *Appl. Catal. A: Gen.* 2011, **406**, 119–123. (f) N. Murakami, S. Kawakami, T. Tsubota and T. Ohno, *J. Mol. Catal. A: Chem.* 2012, **358**, 106–111.
27. For example, our paper: (a) F. Amano, T. Yasumoto, O.-O. Prieto-Mahaney, S. Uchida, T. Shibayama and B. Ohtani, *Chem. Commun.*, 2009, **45**, 2311–2313. Papers from the other groups: (b) M. Miyauchi, *J. Mater. Chem.* 2008, **18**, 1858–1864. (c) D. H. Wang, J. Liu, Q. S. Huo, Z. M. Nie, W. G. Lu, R. E. Williford, Y. B. and Jiang, Y. B. *J. Am. Chem. Soc.* 2006, **128**,

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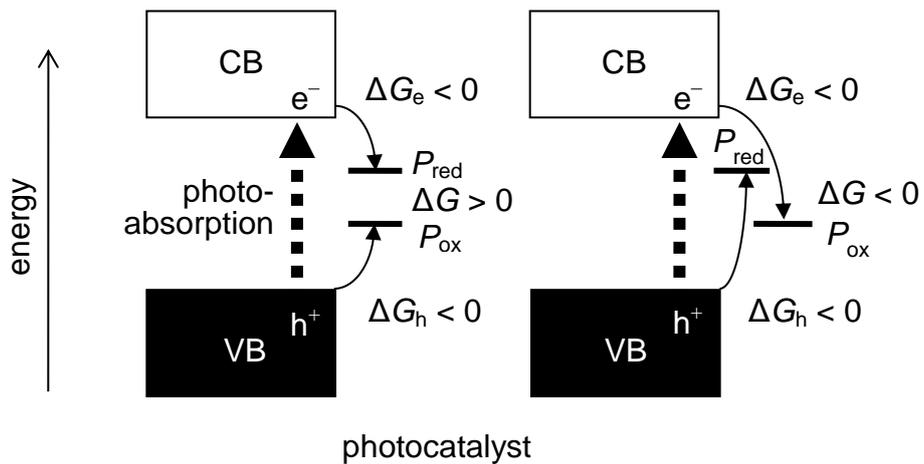


Fig. 1 Electronic structure of semiconductor photocatalysts and Gibbs-energy change in photocatalytic reactions.

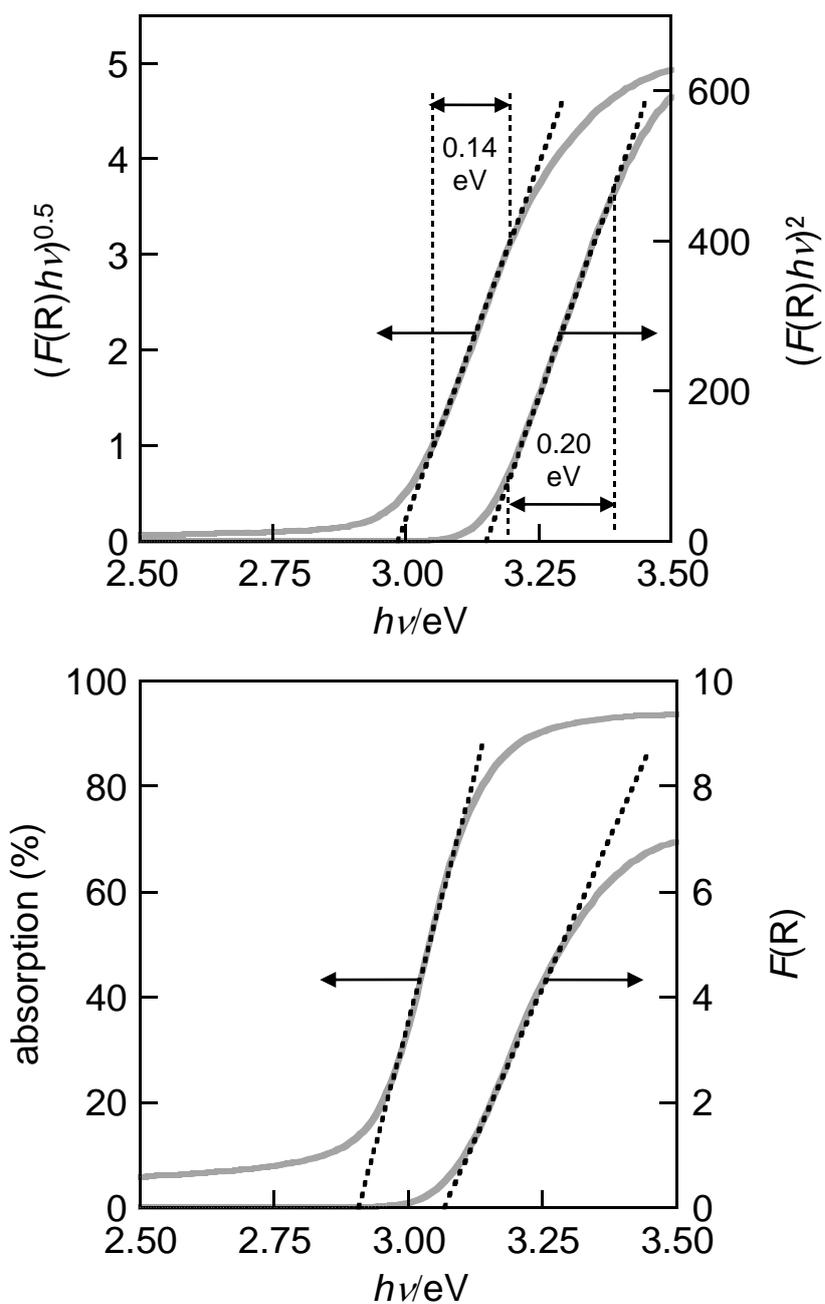


Fig. 2 (upper panel) Two kinds of plots for determination of band-gap energy (E_g) of titania (JRC-TIO-3 calcined at 1173 K). Assumptions of indirect (left) and direct allowed transitions give band gaps of 3.00 and 3.14 eV, respectively. Numbers with the unit of eV show the interval of linear parts. (lower panel) Plots of absorption (extinction) and Kubelka-Munk function ($F(R)$) of the same sample. X-intercepts of lines fitting to the spectra in the absorption edge region are 2.91 and 3.07 eV, respectively. These plots have been shown in the author's recent review (ref. 4).

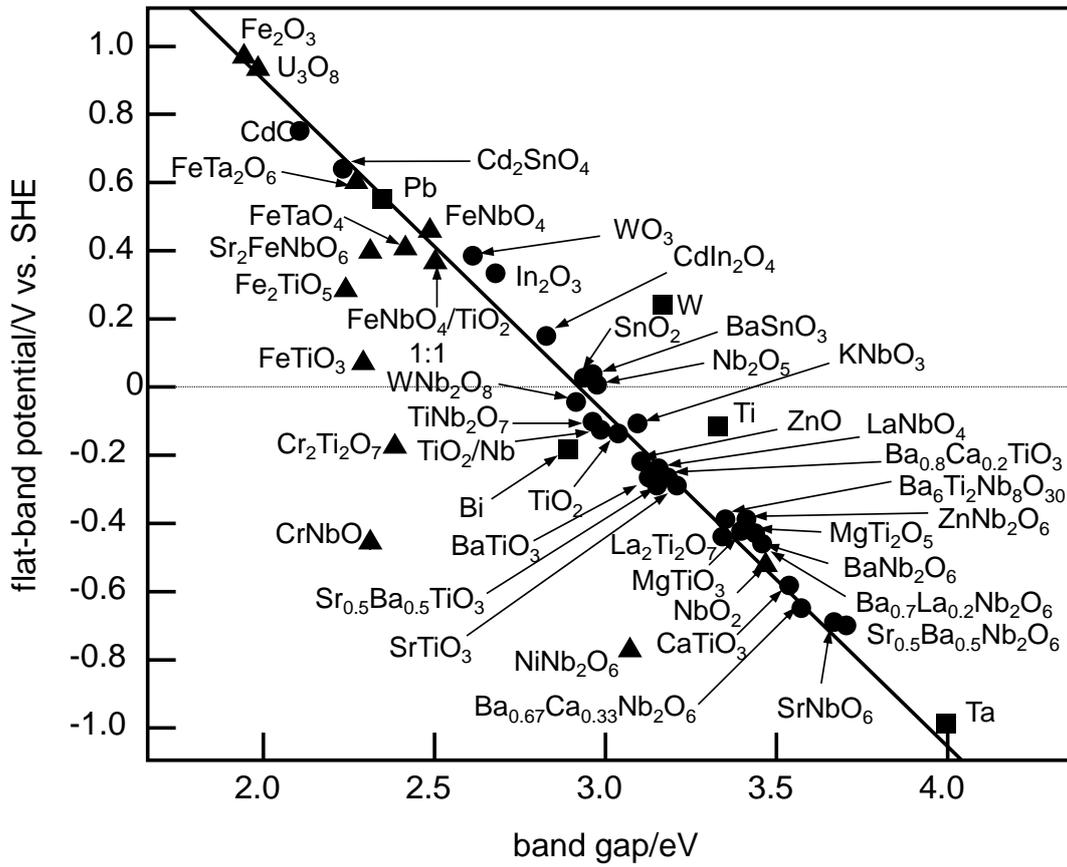


Fig. 3 Scaife's plot reproduced from his original paper (ref. 11). Circles: metal oxide of vacant or filled d-levels, squares: metal oxides prepared by heating of the corresponding metal plates and triangles: metal oxides of partly filled d- levels.

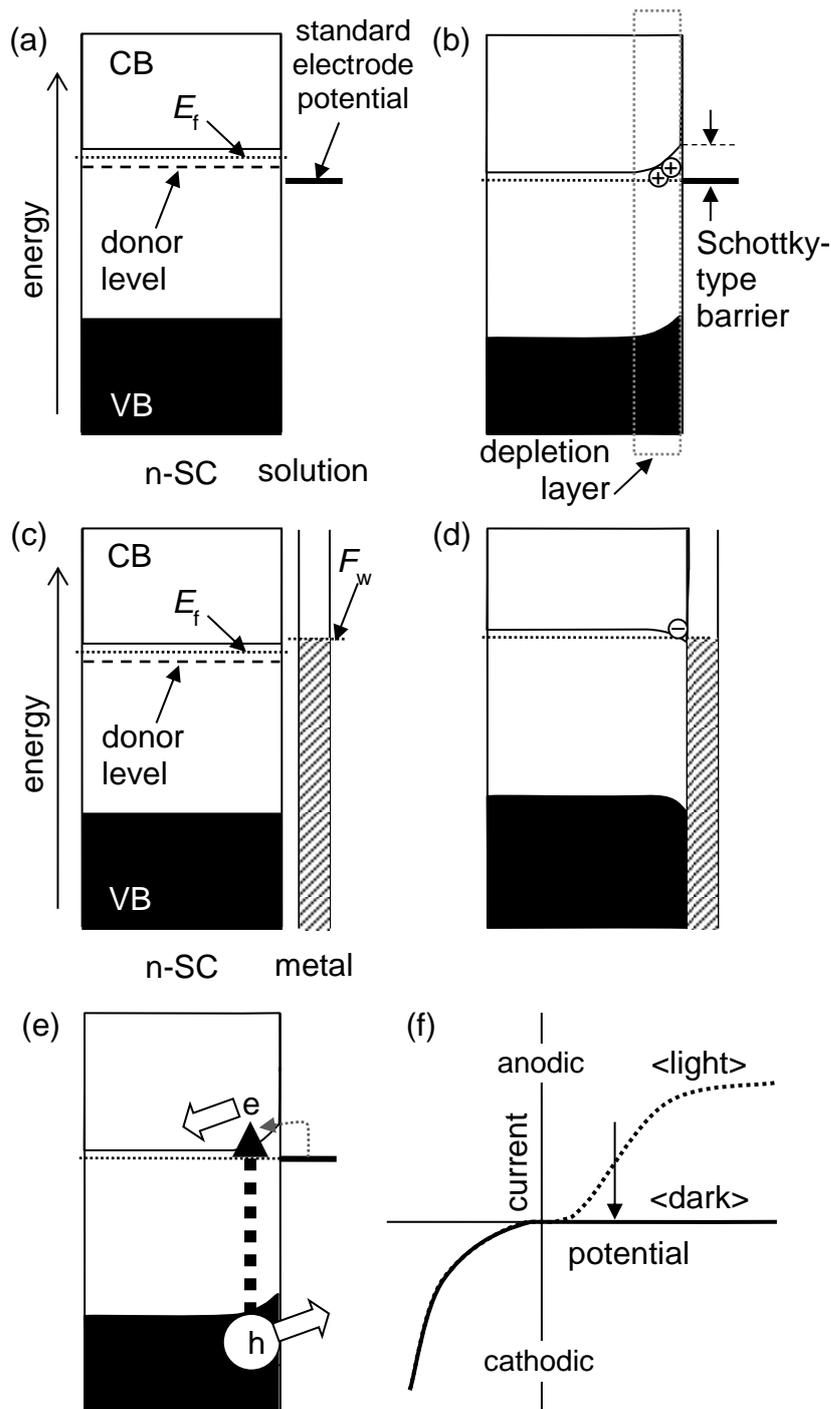


Fig. 4 (a) N-type semiconductor (n-SC) and solution and (b) Schottky-type junction with a depletion layer where electrons in donor levels flow out to the solution to lower the Fermi level (E_f). (c) n-SC and metal with work function (F_w) and (d) ohmic contact between them. (e) n-SC–electrolyte interface under photoirradiation and (f) ideal potential–current plots in the dark and under photoirradiation in an aqueous electrolyte solution. Photoanodic current is detected at the potential more cathodic (left) than the standard electrode potential for water oxidation shown by an arrow.

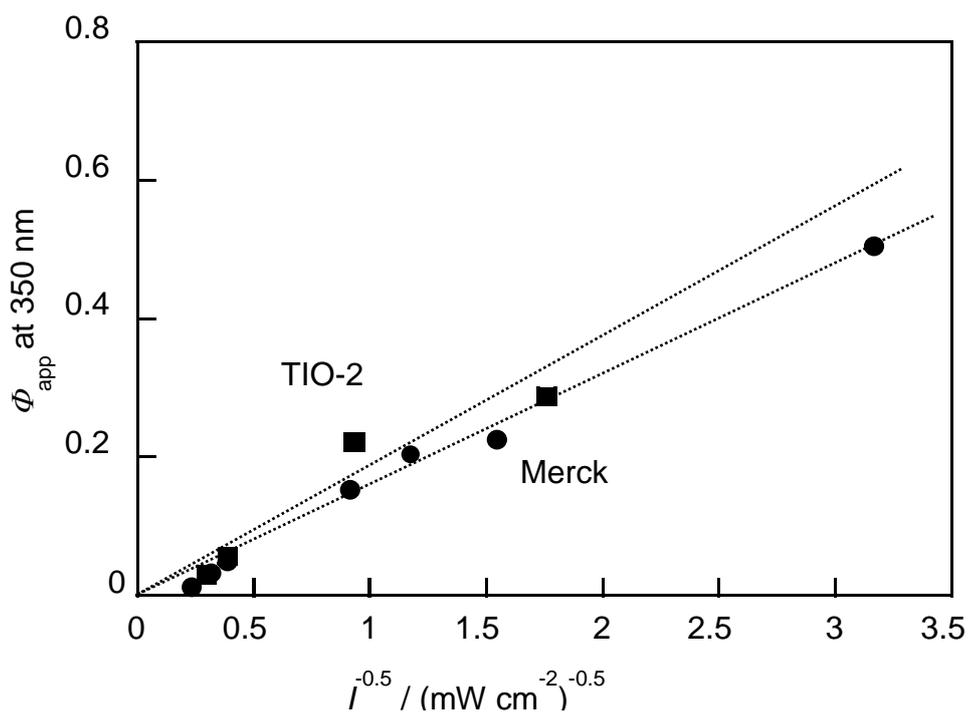


Fig. 5 Plots of apparent quantum efficiency of photocatalytic decomposition of acetic acid in aqueous suspensions of anatase titania particles (JRC-TIO-2 and Merck) as a function of -0.5 th power of intensity of monochromatic light at 350 nm.

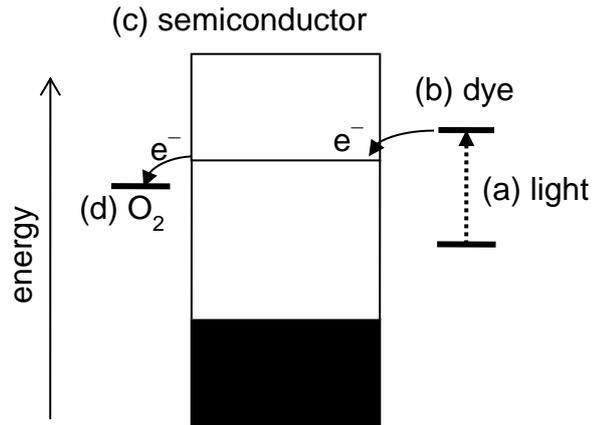


Fig. 6 Possible mechanism of "dye-sensitized" photoinduced oxidative decomposition of dye adsorbed on the solid surface in the presence of oxygen. Components (a)–(d) are necessary conditions for "dye-sensitized reaction" and they are also necessary conditions for ordinary photocatalytic reaction.