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Editorial

Message from the Editor

Since April 2004, *Chemistry Letters* has been publishing *Highlight Reviews*, in addition to traditional *Letters*. To our gratification, the new addition is well regarded as being timely, concise, and of high standards. Very recently, we received a paper that was originally submitted as a manuscript for *Highlight Review*, however, after initial peer review, it seemed to differ in character and size from what we expect for such a publication.

We, the editorial board, discussed whether we should accept this contribution as a *Highlight Review* or whether to reject it. Extensive discussion led to the conclusion, as I announced in the January issue this year, we should add another new class of article, *A Personal Commentary*, which may discuss a variety of contemporary problems encountered in the cutting-edge field of chemistry and may be presented in a manner somewhat different from a typical scientific style. Very young and hot fields of chemistry may experience instability associated with elusive, putative and/or premature concepts, proposals, and experimental techniques.

Accordingly, we consider it advisable for world-wide readers to suggest new ideas and concepts for reducing such uncertainty and to share their suggestions among our readers.

Our first example of *Personal Commentary* is a paper of this kind, which follows this message. Although we do not expect to publish *Personal Commentary* in every issue, we would like to receive and publish this kind of paper from time to time.

Prof. Tamejiro Hiyama
Editor-in-Chief of Chemistry Letters, The Chemical Society of Japan

A Personal Commentary

Preparing Articles on Photocatalysis—Beyond the Illusions, Misconceptions, and Speculation

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Abstract

A growing number of papers on research subjects relating to photocatalysis have and will continue to be submitted and published in scientific journals. Some of these, published or still under review, include illusions and misconceptions that may, from a scientific point of view, adversely affect the writing of academic papers and hamper the development of scientific and technological research in this field. In the present article, the author would like to point out the problems that researchers in photocatalysis encounter when writing articles. In fact, one of the most serious concerns regarding the abstracts contained in most scientific papers is that they often include misleading speculation(s) which are not based on sound scientific evidence yet may be interpreted as truth. A fair number of readers, especially busy ones, may read only the titles and abstracts without serious consideration or analysis of the discussions. Reviewers and editors need to consider such problems, as might be expected, however, the reader community also needs to be instructed of such aspects in order to gain a more correct understanding of what is and is not acceptable. This article aims to present an analysis of such inherent problems in hopes of improving the quality of the research work and scientific papers in this field.

♦ Introduction

It is not surprising that many papers relating to photocatalysis have been published in various scientific journals since it is now recognized as one of the most important sciences in the development of technologies that can improve the quality of life. For example, the decomposition of volatile organic compounds in water or indoor air and the self-cleaning of window glasses and walls can be achieved by photocatalysis. This author has been studying photocatalysis for more than twenty-five years so that such recent developments are exciting and encouraging. During the past decade, many researchers have become involved in the study of photocatalysis. There appear to be at least three reasons for this trend. One is the availability of pressure-resistant bottles made of inert perfluoro polymer which enable hydrothermal synthesis and/or treatment of a wide variety of metal-oxide photocatalysts. The second reason is that photoirradiation of solid materials in the presence of organic compounds and molecular oxygen induces photoreactions that are more or less detectable, though sometimes the reaction is not truly photocatalytic. The third reason is the use of organic dyes as a model compound for photocatalytic decomposition reactions, enabling the feasible determination of photocatalytic activity using only a spectrophotometer and a quartz cell. It is, thus, possible to obtain results on photocatalytic reactions by preparing various solid materials and irradiating them in the presence of organic dyes. The accumulation of data on photocatalysis, e.g., using schemes or tables on the photocatalytic activity for a variety of samples, can lead to the development of high-performance photocatalysts if analyzed in the appropriate way. However, it seems that there is no specific guiding philosophy for such analysis. The inherent and latent problems existing in photocatalytic research may, thus, be reflected in the scientific papers. Considering such issues, the author would like to analyze the various problems which appear in papers on photocatalysis so that, as much as possible, they can be avoided. The author asks also to be forgiven for not citing the specific works used as examples in this article nor showing any figures since the purpose of this article is not to criticize but to learn. Some of the points presented here are well known to veteran scientists, however, the author writes also for the uninitiated and as a reminder to himself. First, the problems seen in introductory sections will be presented.

Definition of "Photocatalysis"

There are various definitions for the term "photocatalysis," however, to save space, a "photocatalytic reaction" can be defined as a chemical reaction induced by photoabsorption of a solid material, or "photocatalyst," which remains unchanged during the reaction. In other words, the solid acts catalytically (without change) under light and this explanation may be consistent with most definitions. "Photocatalysis" is the conceptual name for the photocatalytic reactions. From this understanding, basic data can be obtained by measuring the consumption of the starting materials and/or reaction products initiated by photoirradiation and then examining whether the photocatalyst or its properties have been modified during the reaction. This seems to be a relatively easy procedure. However, various problems are, in fact, encountered when trying to prove a given phenomenon as being photocatalytic, as will be discussed later.

Photocatalysis is often introduced with the aid of a schematic representation of the electronic structures of semiconducting materials, a band model; an electron in an electron-filled valence band (VB) is excited by photoirradiation to a vacant conduction band (CB), which is separated by a forbidden band, a band gap, from the VB, leaving a positive hole in the VB. These electrons and positive holes drive reduction and oxidation, respectively, of compounds adsorbed on the surface of a photocatalyst. Such an interpretation accounts for the photocatalytic reactions of semiconducting and insulating materials absorbing photons by the

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bulk of materials. In the definition given above, however, no such limitation based on the electronic structure of a photocatalyst is included. For example, isolated chemical species, not having the above-mentioned band structure, on or in a solid can be a photocatalyst, and even when a bulk material is used, the photoabsorption and resultant photocatalytic reaction may proceed at a localized site when, for example, photocatalysts are photoirradiated at a wavelength near the band gap (excitation from/to an impunity level). Therefore, the interpretation using a band model is not always adequate for understanding photocatalysis. In this sense, the term "heterogeneous photocatalytic reaction (photocatalysis)" seems better than "semiconductor photocatalytic reaction" based on the electronic band structure.

Catalyst and Photocatalyst

Based on the above definition, photocatalysts absorb light to be excited to a higher energy state, which is similar to a sensitizing molecule working in homogeneous photoreaction systems. Although the sensitizers are not solid, they can be photocatalysts if they are reproduced after photoinduced reaction processes, and a sensitizer has not been and will not been called a "catalyst." However, solid photocatalysts are often called "catalysts." One reason is that some photocatalysts, such as titania (titanium(IV) oxide, TiO_2), have been used as catalysts. Sometimes a material has been called a "catalyst" when the same or similar compounds have been used as catalysts, though the name "catalyst" should be given to a material that catalyzes a chemical reaction. Another possible reason is that some authors have misinterpreted photocatalytic reaction as being a reaction driven by photoirradiation of a catalyst, i.e., a combination of "photo" and "catalyst." Catalysis is, by general definition understood by the author, acceleration of a reaction that proceeds spontaneously from the viewpoint of thermodynamics by reducing the activation energy. Considering that photocatalysis includes reactions that accumulate energy, e.g., water splitting, photocatalysis cannot be included in the category of catalysis and therefore a photocatalyst cannot be called a "catalyst."

Honda–Fujishima Effect

The Honda–Fujishima effect is a well-known chemical phenomenon closely related to photocatalysis.[1] Photoirradiation of a titania single-crystal electrode immersed in an aqueous electrolyte solution induces oxygen evolution from the titania electrode and hydrogen evolution from a platinum counter electrode when some anodic bias is applied to the titania working electrode or chemical bias, e.g., making higher pH of an electrolyte solution for the working electrode, is given. An important point is the requirement of these bias applications in this system. The use of the term "effect" might mean that photoirradiation has an effect on electrolysis of water. Therefore, even when a titania electrode connected to a platinum electrode is assumed to be a photocatalyst, the system cannot be photocatalytic owing to the requirement of bias. Although the author would like to stress that the discovery of the Honda–Fujishima effect is one of the most important discoveries in chemistry and opened up and extensively promoted the research field of photocatalysis, it cannot be an origin of photocatalysis. Actually, reports on photocatalytic oxidation of organic compounds by titania powders had been published[2,3] before the discovery of this effect. In other words, the paper published in *Nature* in 1972 is undoubtedly an origin of research activity of photocatalysis but not an origin of heterogeneous photocatalysis in the bibliographic sense. Therefore, it is scientifically incorrect to state that photocatalytic reaction with titania particles was discovered by Fujishima and Honda in 1972.

Charge Separation

This is a very convenient term when discussing rate or mechanism. Photoexcited electrons and positive holes produced by photoabsorption (It should be noted that an electron-positive hole pair is not produced after photoabsorption; photoabsorption and electron–hole generation are the same phenomenon.) are located near each other and interact with each other by electrostatic force (Strictly speaking, they are not produced at exactly the same position; their positions depend on the extent of corresponding orbitals of the top part and bottom part of VB and CB, respectively.). The term "charge separation" means that an electron and a positive hole are spatially separated from their mutual attraction in an intermediate stage of photocatalytic reaction. The related term "exciton" is a pair of electron and positive hole interacting with each other, and production of an exciton requires less energy of excitation than band-gap excitation. Based on the above definitions of "charge separation" and "exciton," irradiation of light with energy sufficiently higher than the band gap of a photocatalyst will produce pairs of electron–positive hole that are originally charge-separated. Therefore, the use of the term "charge separation" in a story telling with the electronic band structure of a photocatalyst seems a little curious. The author considers electrons and holes to be spontaneously charge-separated in most cases.

In the history of research on photocatalysis, there has been discussion on charge separation due to a space-charge layer at the semiconductor–electrolyte (solution) interface. The space-charge layer is produced at the surface of an n-type semiconducting material when electrons in the filled impurity levels that are located under a Fermi level below the bottom of CB are injected into an electrolyte solution that is in contact with the semiconductor to liberate the positive charge near the surface. Due to this positive charge, the bands are bent upward at the surface. Electrons photoexcited within this charged layer tend to move to the inside (bulk), whereas positive holes move to the surface. Thus, electrons and positive holes are spontaneously charge-separated by the space-charge layer and this has been proved for semiconductor electrodes. However, this is not a case for ordinary particulate photocatalysts, because the depth of the space-charge layer, which depends on the density of impurity levels, is calculated for ordinary metal oxide photocatalysts to be larger than a few micrometers, which is larger than ordinary particle size; the presence of space charge layer is less expected.

Another problem with the term "charge separation" is that it tends to be used for interpretation or speculation of results, e.g., if the rate of photocatalytic reaction is lower than expected, this is attributed to something that disturbs charge separation and, on the other hand, if the activity is claimed to be high, this is attributed to something that enhances charge separation, without showing any proof of how charge separation is disturbed or enhanced. This use of "charge separation" gives

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little information on how the photocatalytic activities are controlled.

Content of Ultraviolet Light in Solar Radiation

Since titania can absorb only ultraviolet light, at a wavelength shorter than ca. 390 nm for anatase titania, many studies to extend this absorption range to the visible light region have been performed in order to utilize solar radiation as an energy source for photocatalysis, as discussed later. For the practical application of photocatalysis using solar radiation and indoor light, such an extension of wavelength range is very important. In the introductory parts of reports, the content of ultraviolet light in solar radiation is often stated to be ca. 3–5% without showing a reference, presumably due to repeated requotations. The author could not find the original paper showing calculation of this content.

Using data on solar radiation at the ground surface in the temperate zone (AM1.5)[4] reported by the American Society for Testing and Materials (ASTM, http://www.astm.org/ASTM), accumulated intensity of ultraviolet light below wavelengths of 380, 390, 400, and 410 nm corresponds to 3.39, 4.05, 4.84, and 6.07%, respectively, of total energy of light of wavelength up to 4000 nm (958 $W m^{-2}$).[5] Considering that the boundary wavelength of ultraviolet light and visible light is ambiguous (since the term "visible" means that one can see the light and the boundary is perceived to be different among individuals), the above-mentioned content, 3–5% (or 3–6%), seems reasonable. The first paper, if it exists, describing this range of ultraviolet light content might have shown a similarly calculated result, and authors of subsequent papers might have referred to this content without citation.

It should be noted that the calculation has been made on the basis of energy of light, not on the basis of number of photons. In discussing energy conversion efficiency, e.g., for solar cells, in which efficiency of conversion of solar energy is significant, content of light of a certain wavelength region should be discussed on the basis of energy. However, photocatalytic reactions except for energy conversion systems, e.g., photosplitting of water into hydrogen and oxygen, do not convert energy. Thus, the energy conversion efficiency cannot be discussed and, instead, quantum efficiency (described below) becomes significant. Under such conditions, the content of light of a certain wavelength region should be calculated or measured on the basis of photon numbers. Energy of a photon in the ultraviolet light region is larger than that in the visible light and infrared light regions and thereby the content calculated on the basis of number of photons must be much smaller than 3–5%.

Is Oxidation Ability of a Titania Photocatalyst High?

It is true that the photocatalytic reaction by titania and related photocatalysts under ultraviolet irradiation in the presence of air or oxygen decomposes organic compounds almost completely, i.e., the compounds are mineralized into carbon dioxide (and water). Actually, this shows that the power of titania photocatalysts driving this chemical reaction is sufficiently high. Related to this, it is stated in many papers on titania photocatalysis that the oxidation ability of positive holes in photoexcited titania particles is very high. Considering the position of the top of the valence band of titania, ca. 3 V vs. NHE (at pH 0),[6] the potential of positive holes seems far more positive than that for oxidation of ordinary organic compounds. However, is this the case for titania only? Roughly speaking, all metal oxides have essentially the same oxidation ability, i.e., the same potential of the top of the valence band, since the valence bands of metal oxides are mainly composed of the same O 2p atomic orbitals; the potential of the conduction band varies depending on the kind of metal, as has been clearly shown by Scaife.[7]

One of the possible reasons for the high activity of titania compared with that of other metal oxides is high reduction ability to inject photoexcited electrons into molecular oxygen adsorbed on the surface of photocatalysts. Since photocatalytic reactions must be completed with consumption of the same numbers of electrons and positive holes, positive holes, even if their potential is sufficiently high, cannot be utilized when photoexcited electrons are not consumed. Among the various metal oxides, titania has a relatively high ability of reduction of oxygen under photoirradiation. In this sense, a plausible explanation is that titania has sufficient ability for electron utilization to drive oxidation by positive holes (or intermediate species produced by them) of high oxidation ability, and other metal oxides with low photocatalytic activity may have low reduction ability even though they also have high oxidation ability. This suggests that improvement of reduction ability and/or modification of the reduction mechanism of metal oxides other than titania may produce a photocatalyst with higher photocatalytic activity under visible light irradiation.

Participation of Hydroxyl Radical and Other Active Species

As intermediate species, hydroxyl radical (·OH), superoxide anion radical ($O_2{\cdot}^-$), hydroperoxy radical ($HO_2{\cdot}$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$) have been proposed since the early stage of research on photocatalysis for photocatalytic reaction systems containing titania as a photocatalyst. Such active species may have a relatively short lifetime, because of the higher reactivity, and therefore in situ detection is not easy. Many studies have shown the presence of such species in photocatalytic reaction systems, but those studies showed only the existence of species, and not their participation in photocatalytic reactions. Even though the amount detected was rather small, it is rather difficult to exclude the possibility of participation of such active species, considering their short lifetime. However, at the same time, it is not so easy to determine the extent of participation of the active species in actual photocatalytic reaction systems. This problem should be discussed considering possible uncertainty in participation of the active species.

Quantum-size Effect

This frequently used term means that when the size (radius) of solid particles becomes smaller than their Bohr radius, the bottom of the conduction band and the top of valence band shift in negative (high electronic energy) and positive (low electronic energy) directions, resulting in expansion of the band gap. The Bohr radius for anatase particles and that for rutile particles have

been estimated to be 2.5 and 0.3 nm, respectively.[8] Preparation of crystalline titania particles of such small size seems to be difficult, and titania particles claimed in papers to show a quantum-size effect might be larger than these sizes. A blue (shorter wavelength) shift, if observed, of the absorption edge of those samples might be due to the amorphous part of titania, not to the quantum-size effect. At least for titania photocatalyst, use of quantum-size effect for interpreting the results seems inappropriate.

♦ Experimental

Identification of Products

Strictly speaking, all of the products of reported photocatalytic reactions must be identified. If authors claim the application of a heterogeneous photocatalytic reaction to synthesis of compounds, isolation and identification of the product(s) are indispensable. Although organic chemists have recognized this as common sense, researchers in other fields of science should be reminded of this to avoid confusion induced when products are reported incorrectly without appropriate identification.

Chromatography cannot be used for identification. Although this is generally noticed, mistakes in identification have been made also in the field of photocatalysis. It should be noted that, as well as this chromatography problem, identification cannot be completed in a strict scientific sense. Accumulation of results that are consistent with the presumed structure of a product shows the consistency but not proof; compounds are always almost identified with the least possibility of another structure.

Use of P25 as a Reference Photocatalyst

Titanium(IV) oxide (TiO_2, titania) is a promising photocatalyst material without any demerits except for a fact that titania can absorb light of wavelength shorter than ca. 400 nm, i.e., ultraviolet light. Empirically, a solid material composed of or including titania shows appreciable photocatalytic activity when irradiated with ultraviolet light, and therefore numerous titania or titania-based samples have been prepared and their photocatalytic activities (Problems in photocatalytic activity tests will be discussed later.) have been examined. Since photocatalytic activity is more or less a relative measure, use of a reference sample for comparison is preferable. Degussa P25 (The official product name is "AEROXIDE TiO_2 P 25"; Nippon Aerosil supplies this in Japan.) is often used as a reference. This sample is supplied widely, and thereby comparison of photocatalytic activity of a given sample with that of P25 is convenient to check the relative activity. In this sense, P25 is one of the best products. An additional merit is that P25 often exhibits higher activity for a wide range of photocatalytic reactions. Actually, in our experience, preparation of titania samples showing activity higher than that of P25 is not easy, and, thereby, when a titania photocatalyst exbilits activity higher than that of P25, it can be claimed that the photocatalyst has high photocatalytic activity. However, it should be noted that the highest activity of P25 is not guaranteed in all photocatalytic reactions. Claiming high activity of a photocatalyst by showing that the photocatalyst is more active than P25 in only one reaction system is insufficient.

The mysterious structure (crystalline content) and photocatalytic activity of P25 and their determination are discussed later.

Determination of Crystal Structure by X-ray Diffraction Analysis

Unlike that in the case of molecules or metal complexes, description of the structures of solid inorganic materials, especially powder samples, is difficult. One of the reasons is that the structural parameters, e.g., particle size, have a wide distribution and thereby preciseness in the measurement strongly depends on the method employed. Another problem is that solids have surfaces that have properties different from their bulk and sometimes have a decisive effect on the reaction occurring on them.

Fundamental structural information of solid materials is their composition. Although in very limited cases, for example, when a solid is not a crystalline material, the solid composition is determined by dissolution and chemical analysis, solid composition is usually determined by X-ray diffraction (XRD) analysis. The solid composition is determined by comparison of peak positions corresponding to lattice spacing with reported values (There are no ways to identify the solid samples used in the measurements of the reported data, and this implies that the identification by XRD is only possible based on the assumption that the reported data are correct.). Thus, a crystalline phase giving XRD peaks can be identified qualitatively. Then, can we measure the content of the crystalline phase quantitatively? As described in the following section, even if only one group of XRD peaks assigned to a single phase of crystalline appears, the possibility of the presence of an amorphous phase, which does not give any XRD peaks, cannot be excluded. Furthermore, if more than two sets of XRD peaks are observed, quantitative measurements are necessary.

It has been suggested that the intensity of the XRD peak is proportional to its content,[9] and this seems to enable quantitative analysis of crystalline contents using appropriate standard samples composed of a single crystalline phase. It seems that there is no guarantee of constant diffraction peak intensity even for high-purity single-phase samples used as a standard.[10] Furthermore, it has been suggested that small anatase crystallites (<30 nm) in anatase–amorphous mixtures give XRD peak intensity which is smaller than that expected on the basis of differential scanning calorimetry (DSC) results.[11] Therefore, it is necessary to make a calibration curve using a standard sample extracted from a given sample of a mixture. As far as the author knows, there have been no reports on such quantitative XRD analyses of samples that had been a crystalline mixture when prepared. Recently, groups of the author and Ohno succeeded in isolation of anatase[12] and rutile[13] crystalline phases, respectively, from P25. This enabled precise determination of the crystalline content of anatase and rutile, assuming the presence of an amorphous titania phase;[14] the ratio of anatase, rutile, and amorphous has been determined to be 78:14:8.[15]

This ratio is different from the frequently described crystalline content of 80% (73%) anatase and 20% (27%) rutile, which was presumably calculated using the equation[16]

$$X_A = 1/(1 + 1.26 I_R/I_A), \quad (1)$$

where X_A is crystalline content of anatase, and I_R and I_A are intensities of the most intense XRD peaks for anatase and rutile, respectively. It should be pointed out that laboratory-made anatase and rutile powders and their mixture were used without any

structural information on the powders, and that the above equation could reproduce only the crystalline content for the artificial mixtures. Actually, crystalline content (anatase and rutile) calculated by the author's group using the above equation was 76:24 or 84:16, with peak height and peak area intensities, respectively. It should be noted that a coefficient "1.26" was determined experimentally. It is thought that the coefficient depends on instruments and standard samples used in the measurements, but this has not been discussed. Furthermore, even if the coefficient is improved, the equation neglects the presence of an amorphous part.

It should be noted that crystalline content in solid samples, at least those containing an amorphous phase, can be determined by XRD analysis only when pure crystalline phases contained in the samples are isolated.[17]

Use of Scherrer Equation

Scherrer's equation is

$$L = K\lambda/\beta\cos\theta, \quad (2)$$

where L, K, λ, β, and θ are size of particles in the direction vertical to the corresponding lattice plane, a constant,[18] wavelength of X-ray, corrected full width at half maximum (FWHM) of the XRD peak, and angle of diffraction, respectively. Since K has been introduced in the derivation of this equation[9] to be 0.891, K has its effective digits. The effective digits of the resulting size of particle L should be one, if "0.9" is used. In order to show the size L with three-digit accuracy, a value of "0.891" should be used. Another notable point is the correction of FWHM. Two kinds of correction are required. One is correction for broadening due to $K_{\alpha 2}$ radiation, and the other is for broadening due to the optical path in the diffractometer. Generally speaking, the former and the latter corrections are made by assuming a radiation intensity ratio of $K_{\alpha 1}$ and $K_{\alpha 2}$ and by using FWHM of a standard large crystalline sample. There are at least three ways for the latter correction, but there seems to have been no discussion on the best way. The simplest way, subtraction of FWHM of the standard, has often been employed. To the author's knowledge both corrections appreciably affect the size of particles; a large error is expected without such corrections. Therefore, when the size of particles is demonstrated, the methods used for FWHM corrections should be described.

As described above, the size of particles in the direction vertical to the corresponding lattice plane can be estimated using Scherrer's equation. In comparison with the data obtained in another way, e.g., transmission or scanning electron microscopy, difference due to this may be observed.

Finally, broadening of FWHM of XRD peaks is also induced by distortion of the crystalline lattice. The Williamson–Hall equation includes this, as well as the effect of particle size.[19] In other words, Scherrer's equation neglects the effect of crystal lattice distortion. For samples that are expected to have a large degree of distortion, analyses using the Williamson–Hall equation should be carried out.

Amorphous Phase and Crystallinity

All solid materials can be categorized into two parts: crystal and amorphous parts. The crystal part has a long-range order of arrangement of atoms, ions, or molecules and the amorphous part has only a short-range order. Empirically, crystals are detected by XRD patterns; peaks appearing in an XRD pattern suggest a certain crystal structure among possible or reported polymorphs, e.g., anatase, brookite, or rutile for titania crystals. On the other hand, there seems to be no direct method to detect amorphous structure; XRD patterns without any appreciable peaks suggest only that the sample is amorphous without any information on its composition, and if some peaks appear, the XRD pattern can not give any information on whether an amorphous part is included or not. This leads to a misunderstanding of solid structure or composition using an XRD pattern. It is difficult and complicated to prove the presence/absence of an amorphous part and, if present, its content.

Strictly speaking, an amorphous phase has a chemical composition the same as its crystal, e.g., amorphous titania must be of TiO_2. However, determination of content of the amorphous part is difficult and has been determined only in the limited cases. In most cases, it was suggested that there was an amorphous part of something, e.g., titanium oxide or titanium hydroxide. For titania samples, an exothermic peak due to the crystallization of amorphous parts into anatase observed in differential scanning calorimetric (DSC) analysis could support the presence of amorphous titania.[11] This is, to the author's knowledge, the only report discussing the content of amorphous phase (presumably of TiO_2) in titania particulate samples and its photocatalytic activity. Though this paper has been cited frequently as a reference for the negligible photocatalytic activity of amorphous titania, there is no guarantee that the structure of the amorphous part is the same as that of a given amorphous part reported in papers.

In relation to the above-mentioned problem of "amorphous," it should be pointed out that the term of "crystallinity" is ambiguous. When this term is defined as extent of crystallization of a certain non-crystalline material, crystallinity is calculated from a (weight) ratio of crystalline and amorphous parts. However, the ratio can be determined only in limited cases in which the crystalline part(s) is (are) isolated to be a standard of quantitative analysis in XRD analysis, since the crystalline content is not always proportional to intensity of the corresponding XRD peak(s) as discussed in the preceding section. Sometimes the term is used to show extent of crystalline growth, e.g., by observing a narrower (sharper) XRD peak. Since the width of an XRD peak is closely related to the size of crystallites (Scherrer's equation discussed in the preceding section), the use of the term "crystallite size" is preferable to "crystallinity" when only the sharpness of an XRD peak(s) is discussed.

Quantum Efficiency and Apparent Quantum Efficiency

Quantum efficiency (quantum yield) is defined as a number ratio of reacted or liberated molecules to absorbed photons. This definition might be appropriate for homogeneous photoreactions in which a photon is absorbed by a molecule to produce a product molecule, i.e., only a one (photon)-by-one (molecule) reaction seems to be presumed (second law of photochemistry). In the heterogeneous photocatalytic reaction, in which multiple numbers of photons are absorbed due to relatively large size of particles compared with molecules, multiple-electron (posi-

tive hole) transfer may occur. For example, photocatalytic silver metal deposition accompanied by molecular oxygen (O_2) liberation proceeds with the following stoichiometry:[20]

$$4Ag^+ + 2H_2O \rightarrow 4Ag + O_2 + 4H^+. \quad (3)$$

For the determination of quantum efficiency, it is necessary to make an assumption on how many photons are required for the reaction. One of the possible and the most frequently employed assumption is that four photons are required for liberation of one oxygen molecule, four silver metal atoms, or four protons, and when the O_2 yield is used, the quantum efficiency is calculated to be

$$4n(O_2)/n(\text{photon}), \quad (4)$$

where n is the number of molecules or photons. Thus, for the calculation of quantum efficiency of heterogeneous photocatalytic reactions, it is reasonable to consider the efficiency of utilization of electrons–positive holes assuming that an electron and positive hole pair is produced by absorption of a photon. However, since neither a photoexcited electron nor a positive hole appears in stoichiometry, the above-mentioned consideration may not always be straightforward. For example, acetic acid dissolved in air-saturated water is decomposed into carbon dioxide by an appropriate suspended photocatalyst with the following proposed stoichiometry:

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O. \quad (5)$$

How many photons are required for this reaction? Assuming that only O_2 is reduced by photoexcited electrons in this reaction and reduction of an O_2 molecule requires four electrons, this reaction is an eight-electron process. However, since the photocatalytic reaction of acetic acid may include a radical chain mechanism or at least addition of O_2 to intermediate radicals, an acetic acid molecule could be decomposed by less than 8 electrons. It is impossible to calculate intrinsic quantum efficiency, i.e., efficiency of utilization of electron–positive hole pairs only from the product yield. Therefore, quantum efficiency is reported with the description that a given reaction is assumed to proceed through a proposed multi-electron process (e.g., 8 for the acetic acid decomposition in eq 5).

Another problem for the determination of quantum efficiency is the difficulty in determining the number of absorbed photons. Unlike measurement for homogeneous solutions, solid materials scatter incident photons to reduce the light intensity arriving at a detector in a spectrophotometer. In the wavelength region in which only some of the photons are absorbed, i.e., around the band-edge wavelength, it is difficult to measure the photoabsorption efficiency (This problem is discussed in the following section.). Therefore, apparent quantum efficiency (photonic efficiency) has often been used instead of quantum efficiency, which is calculated by the number of incident photons rather than the number of photons used for quantum efficiency calculation. Since quantum efficiency is defined as efficiency of electron–positive hole utilization, apparent quantum efficiency is a product of efficiencies of photoabsorption and electron–positive hole utilization. Of course, both quantum efficiency and apparent quantum efficiency depend on the irradiation wavelength and sometimes on the irradiation intensity, and thereby the data should be shown with wavelength and preferably with intensity. In this sense, such measurement must be performed by monochromatic irradiation; irradiation with sharp-cut optical filters is inappropriate.

Photoabsorption by Photocatalysts

It is clear that photoabsorption is one of the most significant steps in photocatalysis and estimation of number (or flux (=rate)) of absorbed photons is an important fundamental experiment, considering the first law of photochemistry, i.e., light must be absorbed by a chemical substance in order for a photochemical reaction to take place. However, as described in the previous section, precise measurements of a photoabsorption spectrum of solid materials are rather difficult.

In the literature, a photoabsorption spectrum, a plot of the extent of absorption as a function of wavelength, has been shown using a unit of absorbance or Kubelka–Munk function. The former, absorbance, is defined as $\log(I_0/I)$, where I_0 and I are intensities of incident and transmitted/reflected light, respectively. When an integrating sphere is used for measurement, I_0 and I are intensities of light detected with and without a given sample of solid material, respectively. However, the use of the unit absorbance does not seem to make sense for solid materials, since this unit is defined for samples having a path length of light transmission; the unit absorbance should be proportional to the concentration of a light-absorbing substance and to the light-path length and, in other words, the concentration in a medium can be calculated from the measured absorbance. On the other hand, Kubelka–Munk (K–M) function is defined as

$$(1 - R_d^2)/2R_d = a/s, \quad (6)$$

where R_d, a, and s are diffuse reflectance ($=I/I_0$), absorption coefficient, and scattering coefficient, respectively. For samples diluted with a medium of less photoabsorption, K–M function can be a measure of the sample concentration. The logarithm of K–M function is often recognized, though this requires assumptions, to be the same as the logarithm of absorption coefficient. Considering the unit of absorption coefficient, cm^{-1}, this corresponds to absorbance of samples of homogeneous solutions or gases. Based on these considerations, both absorbance and Kubelka–Munk function show the extent of the ability of a substance for logarithmic decay of incident light. However, photoabsorption by photocatalysts should be discussed on how much extent of light is absorbed, and absorption, $(I_0 - I)/I_0$, may be most appropriate for comparison with the rate of photocatalytic reaction under irradiation with a given wavelength.

Action Spectrum and Pseudo Action Spectrum

An action spectrum is a plot of apparent quantum efficiency, not quantum efficiency, against wavelength of light used for apparent quantum efficiency measurement; monochromatic light irradiation is required to record an action spectrum. Usually, a grating-type monochromator is used with a light source such as a xenon arc lamp. Interference-type optical filters, transmitting at only a certain wavelength region, are also used for monochromatic irradiation, though wavelengths of possible irradiation are limited. Because of possible dependence of apparent quantum efficiency on light intensity,[21] it is preferable to adjust the light intensity at each wavelength.[22]

Wavelength-selective irradiation can be carried out using

optical filters that transmit light of wavelength longer than a certain limit, i.e., "cut-off filters." Using several filters of different cut-off wavelengths,[23] a plot of apparent quantum efficiency against the cut-off wavelengths can be obtained. This "pseudo action spectrum" resembles an action spectrum obtained by the above-described monochromatic irradiation. However, those are completely different; a pseudo action spectrum is an integrated (from longer to shorter wavelengths) form of a "true" action spectrum based on the assumption that light intensity is constant in the whole range of irradiation, because of the difference in irradiation wavelength region. In other words, the corresponding action spectrum should be estimated by differentiation of the pseudo action spectrum. It should be noted that a horizontal part of a pseudo action spectrum shows that apparent quantum efficiency at the wavelength is negligible even if an appreciable value is seen in the pseudo action spectrum.

♦ Results and Discussion

Among the various problems appearing in papers on photocatalysis, technical problems have been discussed in **Experimental**. Here, in the results and discussion part, problems encountered when photocatalysis and related phenomena are discussed on the basis of experimental results.

Use of Dyes as Model Compounds

Dyes have relatively large photoabsorption (extinction) coefficients (This is the reason why dyes are used for dyes, i.e., coloring agents) and therefore measurements of their concentrations in solutions are easy even if the concentrations are very low. However, the fact that dyes absorb visible light indicates that a photoreaction might be induced by visible-light photoabsorption (dye sensitization) as well as by photoabsorption of a photocatalyst. Although this problem had been pointed out earlier, there have been no clear experimental results showing the self-photodecomposition of dyes, presumably due to the difficulty to show the mechanism of this photoreaction. Actually, determination of the extent to which incident photons are absorbed by a dye and photocatalyst is difficult. The author's group has published a paper showing that methylene blue, the most frequently employed dye, as well as, presumably, other kinds of organic dyes, is inappropriate as a model compound, particularly for testing visible-light-induced photocatalytic activity.[24] There are at least three reasons for its inappropriateness. One is that the dye molecules absorb photons, especially in the visible light range, and thus photoexcited electrons may be injected into photocatalyst particles as has been suggested by the action spectrum similar to the photoabsorption spectrum of the dye. Another reason is that the absolute molar amount of dye contained in the reaction system can be much smaller than that of a solid photocatalyst. The concentration of dye in the solution should be relatively low, since the absorption coefficient is large, as described in the first part of this section. These two facts are closely related to the problem of how we can prove a given reaction to be "photocatalytic," which is discussed in the next section. The third reason is that the mechanism of dye degradation is so complicated that efficiency of the photocatalytic reaction, e.g., quantum efficiency, cannot be measured.

Measuring the consumption (decrease) of a dye during photoirradiation requires only a spectrophotometer, but the use of dyes as model compounds is inappropriate, and, if dyes are used, care must be taken in the analysis of experimental results.

Control Experiments as Proof of Photocatalytic Reaction

Since a photocatalytic reaction is driven by electron–positive hole pairs and a photocatalyst must not be changed during the reaction, the following two sets of experimental results are required to prove that a given reaction is photocatalytic: (1) results showing that the reaction proceeds only in the co-presence of a photocatalyst and reaction substrate(s) under photoirradiation and (2) results showing that a solid material is not changed or modified during the reaction or showing that the molar amount of the product exceeds that of the photocatalyst. For example, if a particulate material is prepared and its reactivity when suspended in a dye solution under photoirradiation is examined, it should be shown to claim that a photocatalytic reaction has occurred that irradiation of the dye solution without the particles and stirring the dye solution in the dark with suspended particles induce negligible decreases in the dye concentration. Are these results sufficient to prove photocatalysis? The answer is "No." As described in the previous section, dyes can inject their photoexcited electrons into solid particles, especially those of titania, and this "non-photocatalytic" reaction proceeds in the co-presence of a dye and solid particles and with photoirradiation. Therefore, the above-mentioned control experiments cannot exclude the possibility of this dye-sensitization mechanism. Thus, there are no general procedures for control experiments. A better, but not complete, way to show that a given reaction is induced by photoexcited electron–hole pairs is to show that the action spectrum (see **Experimental**) resembles the absorption (diffuse reflectance) spectrum of a given solid material.

Checking the turnover number is also important. In order to prove that a solid material works as a photocatalyst, it must be shown that the solid does not change during the reaction or that the molar amount of the product exceeds that of the solid material. In the latter case, the molar ratio of a product to a solid is called turnover number, and if the reaction is stoichiometric, the turnover number should be below unity. Care should be taken regarding this point, especially for photocatalytic reactions of degradations of organic dyes. Since, as mentioned above, the photoabsorption coefficient of dyes is generally large, e.g., $> 10^5\,\mathrm{mol^{-1}\,L\,cm^{-1}}$, the concentration can be $10^{-5}\,\mathrm{mol\,L^{-1}}$ and the absolute molar amount can be 10^{-7} mol when the volume of the solution is 10 mL. Sometimes, two-order of magnitude larger molar amount of a solid material (photocatalyst) in a few-tens of milligram is used, and in these cases it is impossible to show the turnover number larger than unity.

Photocatalytic Activity

Most authors, including the present author, use the term "photocatalytic activity," but in almost all cases the meaning is the same as that of reaction rate. The reason for using the term "photocatalytic activity" may be to make readers think it is one of the properties or abilities of a photocatalyst, i.e., photocata-

lysts have individual activity, while "reaction rate" seems to be one of properties of a reaction system.

In the field of catalysis, "catalytic activity" has been used to show a property or performance of a catalyst, since an "active site" on a catalyst accounts for the catalytic reaction and the reaction rate per active site can be estimated, which should be "catalytic activity." On the other hand, there are no active sites on a photocatalyst,[25] and the reaction rate strongly depends on the irradiated light intensity. Considering that the dark side of a photocatalyst or suspension does not work for the photocatalytic reaction, the use of the term "active site" is inappropriate, and a relationship of photocatalytic activities with active sites therefore cannot be expected.

Rate of photocatalytic reaction, r, can be interpreted in the most simplified form as follows:

$$r = I\phi k_{\mathrm{red}} C_{\mathrm{red}} / (k_{\mathrm{red}} C_{\mathrm{red}} + k_{\mathrm{r}}), \quad (7)$$

where I, ϕ, k_{red}, C_{red}, and k_{r} are incident light flux, photoabsorption efficiency, rate constant of reaction of electron–positive hole pairs with surface-adsorbed substrate,[26] surface concentration of the reaction substrate, and rate constant of electron–positive hole recombination, respectively. Here, the rate equation is analyzed to extract intrinsic parameters, i.e., only those depending on the photocatalyst. The intensity I is an extrinsic (experimental) factor and the photoabsorption coefficient ϕ is an intrinsic parameter depending on the photocatalyst and irradiation wavelength. As stated in the previous section, quantum efficiency is the ratio of reaction rate and absorbed photon flux, $I\phi$. Since quantum efficiency, $r/I\phi$, in an ordinary photocatalytic reaction system has been reported to be much lower than unity, it is assumed that $k_{\mathrm{red}} C_{\mathrm{red}} \ll k_{\mathrm{r}}$. Consequently, equation 7 is further simplified to be

$$r = I\phi k_{\mathrm{red}} C_{\mathrm{red}} / k_{\mathrm{r}}. \quad (8)$$

In this equation, I, ϕ, and C_{red} can be measured or estimated by photometry, spectrophotometry, and adsorption analysis, respectively. Therefore, the ratio $k_{\mathrm{red}}/k_{\mathrm{r}}$ can be extracted from the actual rate. Considering that this ratio does not contain factors or parameters that depend on the reaction conditions, the ratio $k_{\mathrm{red}}/k_{\mathrm{r}}$ (or its product with ϕ; $\phi k_{\mathrm{red}}/k_{\mathrm{r}}$) may be one of the possible measures of intrinsic photocatalytic activity.[27] Assuming further that the rate constant of electron–hole pair reaction, k_{red}, is not changed in a series of photocatalyst samples, the ratio can be a relative measure of rate constant for electron–hole recombination.

Langmuir–Hinshelwood Mechanism

The term "Langmuir–Hinshelwood mechanism" has been used in discussion of the mechanism of photocatalytic reaction in suspension systems, but, as far as the author knows, there has been no definition given for the Langmuir–Hinshelwood (L–H) mechanism in photocatalytic reactions. In most cases, authors have claimed that a photocatalytic reaction proceeds via the L–H mechanism when a linear reciprocal relation was observed between the reaction rate and the concentration of reaction substrate in a solution. These experimental results seem consistent with eq 8 when the substrate is adsorbed by a photocatalyst obeying a Langmuir isotherm and the adsorption equilibrium is maintained during the photocatalytic reaction, i.e., the rate of adsorption is faster than that of the reaction with electrons or holes. Such a situation is often called "light-intensity limited," i.e., photoabsorption is the rate-determining step.[28] The original meaning of the term "Langmuir–Hinshelwood mechanism" in the field of catalysis is, to the author's knowledge, a reaction of two kinds of molecules proceeding on a surface in which both molecules are adsorbed on the same surface adsorption sites and the surface reaction being the rate-determining step. Of course, the general rate equation for the L–H mechanism (not shown here) includes two sets of parameters for two kinds of molecules, and when one set of parameters is neglected, the equation is for a monomolecular reaction, similar to the photocatalytic reaction of a substrate adsorbed in Langmuirian fashion. However, at least in the field of catalysis, the term L–H mechanism is rarely used for such monomolecular surface reactions, since the L–H mechanism has been discussed for a bimolecular surface reaction by comparing with the Rideal–Eley mechanism, in which a surface-adsorbed molecule reacts with a molecule coming from the bulk (outside).

Even if the L–H mechanism is defined as the reaction of surface-adsorbed substrate obeying a Langmuir isotherm being the rate-determining step, the frequently reported experimental evidence, a reciprocal linear relation between concentration of the substrate in solution and rate of photocatalytic reaction is not always proof of this mechanism. From the linear plot, two parameters are calculated. One (often shown as "k") is a limiting rate of the reaction at the infinite concentration giving maximum adsorption, and the other (often shown as "K") is an adsorption equilibrium constant. The former parameter contains a rate constant and adsorption capacity of a photocatalyst, and this may be a photocatalytic activity. The latter parameter shows the strength of adsorption and must be the same as that estimated from an adsorption isotherm measured in the dark. If the kinetically obtained K is different from that obtained in dark adsorption measurement, the L–H mechanism cannot be adopted. Therefore, dark adsorption measurement is always required.

Another point to check is adequate use of the substrate concentration in analysis. Since a Langmuir isotherm is derived on the basis of the adsorption equilibrium between species adsorbed and desorbed in solution, the isotherm is a function of concentration of the adsorbate (molecules to be adsorbed on surfaces) in solution, not concentration of adsorbate in feed. Therefore, the actual concentration, which must be reduced from that in feed due to appreciable adsorption, must be measured at least before photoirradiation. The above-mentioned reciprocal plot for the Langmuirian adsorption analysis is one of the linearization methods and the results are influenced more by the data in a lower concentration part. Analysis using concentration in feed, not that in equilibrium, may give a large error, since relative concentration change by adsorption is large in the lower concentration region.

First-order Kinetics

In many articles, the above-mentioned L–H mechanism has been discussed using rate of photocatalytic reaction with various concentrations of a reaction substrate. On the other hand, "first-order kinetics" has tended to be discussed for time-courses of reaction, and resultant (pseudo) first-order rate constants were compared for different kinds of photocatalysts. In practice, the

logarithm of the concentration of substrate (or product) or its equivalent is plotted against time of reaction, i.e., photoirradiation, and the slope (absolute value) of a linear relation, if obtained, corresponds to (pseudo) first-order rate constant. This analysis is very convenient, since any data, even those measured in arbitrary units, can be used and the same rate constant is obtained as long as the value is proportional to the actual concentration.

First-order kinetics is based on the assumption that the rate of a reaction at a given time is proportional to the concentration of the substrate in solution, which is consistent with actual rate of reactions in homogeneous phase; if this first-order kinetics is adopted to the surface reaction such as a photocatalytic reaction, the concentration used for the analysis must be that of adsorbed substrate, not that in solution. Analysis of reaction rate using a Langmuir adsorption isotherm, discussed in the preceding section, includes this first-order kinetics for adsorbed substrate. Therefore, first-order kinetics using concentration in solution is inconsistent with the rate expression using Langmuir adsorption isotherm. However, papers claiming L–H mechanism using data on reaction rates under the conditions of various substrate concentrations and, at the same time, first-order kinetics using data on concentration in solution observed in time-course curves. If both kinetic analyses are correct, these results should be interpreted as follows. In the relatively lower concentration range of the Langmuir isotherm, the amount of adsorbed substrate is almost proportional to the concentration in solution, i.e., a Henry-type adsorption isotherm,[29] resulting in a linear relation between concentration and reaction rate. Under these conditions, the adsorption equilibrium is maintained during the photocatalytic reaction. However, this should not be described as Langmuirian fashion.

Another possible explanation of first-order kinetics using concentration in solution is that the reaction is diffusion-limited; the surface concentration is always zero and substrate arriving at the surface immediately reacts. The rate of diffusion is proportional to the solution concentration and thereby a linear relation between the rate and the solution concentration can be obtained. However, it is clearly inconsistent with the L–H mechanism assuming a surface-reaction-limited process.

The rate of diffusion of the substrate may be proportional to the surface area of a photocatalyst based on the assumption that thickness of the diffusion layer is so small that the area of cross section of diffusion is almost the same as the surface area. Therefore, a positive correlation between rate of photocatalytic reaction and specific surface area of a photocatalyst is often observed under both diffusion-limited and surface-reaction-limited conditions.

Structure–Photocatalytic Activity Correlation

Almost all researchers, including the author, in this field probably believe that there are certain correlations between structure and photocatalytic activity, and efforts are being made to clarify such correlations in order to design and prepare highly active photocatalysts. One of the clarified points worth noting is that difference in photocatalytic activity cannot be interpreted using only a single property, parameter, or structural description of photocatalysts. For example, the photocatalytic activities could not be explained only by crystalline phase, anatase and rutile, specific surface area, or particle size, observing that the activity differs by more than two orders of magnitude even if the photocatalysts are of the same crystalline, and particles of similar particle size and specific surface area show different activity due to other properties, such as their shape and crystalline content, while we do not know which properties of photocatalysts are significant and how many parameters are required for the description of photocatalytic activities.

Before starting discussion on structure–photocatalytic activity correlations, it should be noted that photocatalysts prepared and/or post-treated in different ways or under different conditions may show different activities, and it is difficult to attribute such difference to the difference in expected and/or observed properties.[30] For example, even if a laboratory-prepared photocatalyst sample of extraordinary large specific surface area shows activity higher than that of samples of ordinary surface area, the correlation between specific surface area and photocatalytic activity is only an empirical one unless it is clarified how the difference in surface area influences the rate expression.[31] Some papers have claimed that the extraordinary shape of photocatalyst particles, such as micrometer-scale length or large platelike crystallites, which is observed by scanning electron microscopy, accounts for the observed activity being different from that in the case of photocatalyst particles of ordinary shape. However, such description is neither scientific explanation nor speculation, since there is no proposal on why and how such shape of crystallites is related to the rate expression. It should be reminded that unknown or unmeasured properties may directly determine the rate of photocatalytic reactions.

Visible-light-induced Photocatalytic Activity

Many efforts have been made to design and develop photocatalysts that work under visible-light irradiation. Strategies that have usually employed in such studies are modification (doping) of titania to give visible-light absorption or use of colored mixed metal oxide and nitride. Although it is expected that such doping of crystalline and mixed metal oxide/nitride may induce production of lattice defects, which enhance the electron–hole recombination, resulting in lower photocatalytic activity, discussion of the strategies is not a purpose of this article. Some problems in the discussion on visible-light-photocatalytic activity are summarized here.

First, the boundary wavelength between ultraviolet light and visible light should be defined. As described in **Introduction**, the meaning of the term "visible light" is light that can be seen, and the limiting wavelength differs among individuals. Many studies demonstrating that visible-light-induced, as expected, photocatalytic reaction used the condition of photoirradiation through an optical cut-off filter, L-42 or its equivalent, and the irradiation wavelength under such conditions used to be described as "$>$420 nm." However, this is inadequate, since this filter transmits light of wavelength $>$ca. 390 nm. Actually, in the author's experience, appreciable photocatalytic activity of anatase titania photocatalysts could be observed by irradiation through the filter. When this optical filter is used for irradiation, comparison of the photocatalytic activity with a representative titania photocatalyst, such as P25 or ST-01 (Ishihara Sangyo), is preferable. Otherwise, optical cut-off filters of longer transmission limits should be used. One of the possible and smart ways is

to define "visible light" as light that negligibly drives photocatalytic reaction by titania and to use an appropriate optical filter to realize this.

Showing that a certain reaction proceeds under the abovementioned visible-light irradiation conditions is not proof of visible-light-induced photocatalytic activity, as explained in the section "*Use of dyes as model compounds*." Then, what experimental results are needed to show that a given photocatalyst can drive the photocatalytic reaction under the conditions of visible-light irradiation? In the author's experience, it is preferable to show an action spectrum, not "pseudo" action spectrum, that resembles a photoabsorption (diffuse reflectance) spectrum (see "*Action spectrum and pseudo action spectrum*"). When an action spectrum is measured, any reaction can be employed as a model reaction, but it is preferable to use a reaction for which the stoichiometry has been clarified. Without showing action and photoabsorption spectra, it is rather complicated to prove that the reaction is a photocatalytic one under the conditions of visible light irradiation.

Photoinduced Superhydrophilicity

An interesting phenomenon related to photocatalysis is photoinduced superhydrophilicity of the surface of a photocatalyst, especially titania thin films. This phenomenon has been proved to occur by photoirradiation, presumably excitation of a photocatalyst through band-gap transition.[32] The hydrophilicity and hydrophobicity of the surface are usually analyzed by water contact angle (WCA) measurement. It is well known that WCA depends strongly on the chemical composition, as well as the morphology, of the outermost surface. Since the molar amount of chemicals of a monolayer of the outermost surface is quite small and since keeping the outermost surface clean and/or controlled seems almost impossible due to contamination from air, analysis of the photoinduced hydrophilicity requires delicate and careful treatments compared with ordinary chemical analytical methods. Furthermore, photocatalytic decomposition of surface-adsorbed contaminants proceeds, at the same time, accompanied by reduction of molecular oxygen.

There is no space for discussion on the photoinduced hydrophilicity and this section is closed only by stating that careful data treatment, analyses, and discussion are required.

Anatase and Rutile

One of the most frequently asked questions is which has better photocatalytic activities: anatase and rutile. There appears to be no adequate answer to this question. As described in **Experimental**, identification of particulate samples is scientifically impossible; even if a large number of measured properties are the same for two samples, there is still a possibility that they have different unknown/unmeasured properties. In this sense, there are no representative anatase or rutile samples for which photocatalytic activities can be discussed.

Empirically, in the photocatalytic reaction in which molecular oxygen is reduced by a photoexcited electron, samples containing anatase crystallites show higher activity than that of samples containing only rutile crystallites. However, in some photocatalytic reactions, the order of activity is reversed. We sometimes see statement such as "In this photocatalytic reaction, Sample A (anatase) prepared by Procedure A showed higher activity than that of Sample B (rutile) prepared by Procedure B. This is attributed to their crystal structure, anatase and rutile, respectively, the former of which is better than the latter." This should read "In this photocatalytic reaction, Sample A prepared by Procedure A showed higher activity than that of Sample B prepared by Procedure B. This trend is similar to reported results for similar photocatalytic reaction systems showing that anatase had higher activity than that of rutile, though the reason for this is still not clear."

Titania has crystal structures other than anatase, rutile and brookite,[33] e.g., TiO_2(B). Strictly speaking, anatase, rutile and brookite are three known polymorphs of "naturally occurring" titania samples out of all polymorphs of titania including artificial ones.

Synergetic Effect

The term of "synergetic effect" in photocatalysis could be defined as follows: when more than two kinds of photocatalysts are used as a mixture, the overall photocatalytic activity exceeds the sum of activities of each photocatalyst. When certain component alone is not a photocatalyst and a mixture with another photocatalyst shows improved activity, that component should be called "co-catalyst" or "enhancer," and the improvement cannot be attributed to a synergetic effect. One of the representative discussions on the synergetic effect is for anatase–rutile mixed crystalline photocatalysts, such as Degussa P25. The author thinks that a synergetic effect has not yet been proved for P25, and the effect seems to be speculation. This is natural considering that each component, anatase and rutile, in P25 had not been isolated before the isolation of anatase by the author's group.[12,15] Even if all of the components are isolated from the mixture, how can we show a synergetic effect? Taking into consideration the fact that a photocatalytic reaction proceeds by photoabsorption of photocatalysts and the fact that total number of absorbed photons is not directly proportional to the mass (volume) of photocatalyst, a control experiment using each component should be carried out with adjustment to make the flux of absorbed photons the same as that for the mixture. However, discussion is still needed to establish a method to clarify the synergetic effect in photocatalysis.

♦ Conclusion

The problems that exist in papers on photocatalysis can be divided into two categories: one is manuscripts that are written in the wrong style while the other is discussions based on illusions, misconceptions, and speculations. The latter has been detailed in this article. Although the author does not know how frequently such problems are found in papers in fields other than photocatalysis, an underlying reason for these problems may be that the history of this research area is shorter than that of the other relating fields. Analyses of the materials, phenomena, mechanisms, and reactions involved in photocatalysis cover a wide range of areas and are not limited to a single research field, thus, a wide background and much experience are necessary to present valid discussions. A fundamental understanding of the scientific background of the various experiments, calculations, data processing methods, and investigative techniques as well

as other details may be necessary in avoiding the issues described here.

An example of the problems arising from variations in writing style can often be found in the conclusions section. Generally speaking, the conclusions presented in scientific papers, not only in photocatalysis, should not simply be a summary or a copy of the abstract. The author thinks that the conclusions should interpret how the reported research work has solved or addressed the unresolved issues presented in the introduction. Authors should, thus, always refer to the introductory section in writing the results and conclusions of their work. In fact, according to the style guide[34] of the American Chemical Society, "The purpose of the conclusions section is to put the interpretation into the context of the original problem. Do not repeat discussion points or include irrelevant material. Conclusions should be based on the evidence presented."

In conclusion, this review has covered the problems found in articles in the field of photocatalysis, although only the most significant points have been discussed. Since this unconventional review may, of course, also include illusions, misconceptions, and speculations, any critiques will be appreciated. Finally, the author hopes that by shedding light on such aspects of writing scientific papers, more vigorous discussions on improving the quality of the work and research in this field will ensue.

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References and Notes

1 A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37. Although the order of author names in this paper is Fujishima and Honda, the order in the term "Honda-Fujishima Effect" is reversed. Many authors, including the present author, have mistakenly cited this paper as "K. Honda, A. Fujishima, . . .". It is important when making **References and Notes** to refer to papers correctly and checking a copy of the paper every time when citing is preferable, though some recent editing systems of scientific papers check the bibliographic data to give direct Internet links. The author hopes that this service does not accelerate the trend of not checking original copies of cited papers.

2 S. Kato, F. Masuo, *Kogyo Kagaku Zasshi* **1964**, *67*, 42. This paper reported photocatalytic oxidation of tetralin (1,2,3,4-tetrahydronaphthalene) by a titania suspension. Although, a paper was referred to as a preceding paper reporting titania photocatalysis (G. F. Huttig, *Kolloid Z.* **1943**, *106*, 166), the paper (Actually, the authors are G. F. Hüttig and W. Kunda) written in German does not seem to report titania photocatalysis.

3 I. S. McLintock, M. Ritchie, *Trans. Faraday Soc.* **1965**, *61*, 1007. In this paper, solid–gas phase photocatalytic oxidation of ethylene and propylene in the presence of adsorbed oxygen on titania is described. This seems to be the first paper on gas-phase titania photocatalysis written in English, though some studies had been reported on photoadsorption/photodesorption of molecules on a titania surface before this paper. Such gas-phase photocatalytic reaction by zinc oxide (ZnO) had been reported before this paper, e.g., Y. Fujita, *Shokubai* **1961**, *3*, 235.

4 http://rredc.nrel.gov/solar/spectra/am1.5/

5 The value $1000\,\mathrm{mW\,m^{-2}}$ is usually used in Japan as the total energy of AM1.5 radiation based on JIS C8911 (http://www.jisc.go.jp/app/pager?id=57836), while the total energy calculated using the table of ASTM is ca. $958\,\mathrm{mW\,m^{-2}}$. The difference is presumably attributable to the difference in instruments used for the measurements.

6 Although estimation of electronic structure of photocatalyst particles is very important, no reliable method for this estimation has been established. The following paper is cited as a reference of electronic structure of anatase (and rutile): L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, H. J. Scheel, *J. Am. Chem. Soc.* **1996**, *118*, 6716.

7 D. E. Scaife, *Sol. Energy* **1980**, *25*, 41. Although this paper clearly showed that the top of the valence band is constant for a large number of metal oxides, including mixed metal oxides (Only five out of more than fifty metal oxides have different valence-band positions.) and this paper is well known by researchers in this field of photocatalysis, there have been some published papers with figures showing different valence-band positions.

8 Y. Nosaka, A. Nosaka, *Nyumon Hikarishokubai (Japanese)*, Tokyo Tosho, Tokyo, **2004**, p. 59.

9 H. P. Klug, L. E. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed., Wiley, New York, **1974**, p. 531. Although this book covers the theoretical background and experimental techniques of XRD measurements with detailed descriptions, the book seems not so popular in Japan, presumably because it has not been translated into Japanese.

10 Actually, peak intensity depending on the size of particles of silica has been reported: I. Nakai, F. Izumi, *Funmatsu X-Sen Kaisetsu no Jissai (Japanese)*, Asakurashoten, Tokyo, **2002**, p. 116.

11 B. Ohtani, Y. Ogawa, S. Nishimoto, *J. Phys. Chem. B* **1997**, *101*, 3746. Presumably, this is the only paper on the negligible photocatalytic activity of amorphous titania.

12 B. Ohtani, Y. Azuma, D. Li, T. Ihara, R. Abe, *Trans. Mater. Res. Soc. Jpn.* **2007**, *32*, 401.

13 T. Ohno, K. Sarukawa, M. Matsumura, *J. Phys. Chem. B* **2001**, *105*, 2417.

14 T. Ohno, K. Sarukawa, K. Tokieda, M. Matsumura, *J. Catal.* **2001**, *203*, 82.

15 R. Abe, D. Li, Y. Azuma, B. Ohtani, to be submitted. B. Ohtani, R. Abe, Y. Azuma, T. Ihara, 17th MRS-J Academic Symposium, Tokyo, Japan, December 10, 2006, Abstr. No. F-16. It should be noted that this ratio is valid only for the sample stored in a cabinet in the author's laboratory. There is no guarantee that all samples of P25 have the same crystalline content.

16 R. M. Spurr, H. Myers, *Anal. Chem.* **1957**, *29*, 760. This very old paper has been digitalized and uploaded on the web site of American Chemical Society. A check of the frequency of

citation of this paper in "Web of Knowledge" showed that this paper has been cited more frequently in past few decades than in the period just after publication. It seems that authors of recent papers on titania photocatalysts have referred to this paper without reading the original copy.

17 While Rietveld method has recently been used for analysis of XRD patterns, the author thinks that this method can not also be used for determination of crystalline content of samples containing an amorphous (not giving XRD peaks) phase.

18 Sometimes this coefficient is called "shape factor," but the author does not know the reason for this.

19 The original paper on this plot is G. K. Williamson, W. H. Hall, *Acta Metall.* **1953**, *1*, 22. The author has not checked discussion, if any, on this plot following the original paper.

20 This stoichiometry has been clarified for the first time by the author's group and reported as S. Nishimoto, B. Ohtani, H. Kajiwara, T. Kagiya, *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2685. Before submission to this journal, the author submitted a part of the experimental results to Chemistry Letters as the first paper in the author's career in the field of photocatalysis, but the paper was rejected presumably due to a reviewer's comment that the content had been reported in a Russian journal without showing bibliographic data (This could not be found.). To submit the results as a full paper, additional experiments were carried out to support the stoichiometry. For example, an oxygen-isotope experiment was carried out and showed the origin of molecular oxygen to be water. As a result, the paper could be published, and it has been cited more than 70 times, including recent citations. This is an example of rejection of a submitted paper not always being disadvantageous for the authors.

21 T. Torimoto, Y. Aburakawa, Y. Kawahara, S. Ikeda, B. Ohtani, *Chem. Phys. Lett.* **2004**, *392*, 220. This paper showed that the rate of photocatalytic reactions in the presence of molecular oxygen, i.e., photocatalytic oxidative decomposition, may strongly depend on the intensity of light irradiation, while the rate of reactions in the absence of oxygen seems to be almost independent of the light intensity.

22 Strictly speaking, when apparent quantum efficiency is discussed, the light intensity should be adjusted to be the same in number of photons, not in energy.

23 In the Japanese Industrial Standards (JIS B7113, discontinued), limiting transmission wavelength is defined as the center of wavelengths giving 72% and 5% transmission. For example, the limiting transmission wavelength for an Asahi Technoglass L-42 cut-off filter is 420 nm based on the standard, and this filter transmits ca. 60% at 420 nm. The figure "42" shows only that 420 nm is the limiting transmission wavelength defined in JIS, and practically >390 nm irradiation is made using this filter. Statements such as "visible-light irradiation at >420 nm was performed using an optical sharp cut filter" seem misleading when L-42 has been used.

24 X. Yan, T. Ohno, K. Nishijima, R. Abe, B. Ohtani, *Chem. Phys. Lett.* **2006**, *429*, 606. Citation of this paper is not expected at all (and actually so), since authors using methylene blue (MB) as a model compound for photocatalytic reaction never want to refer to this and, on the other hand, those who do not use MB need not to refer to this. However, the author's friend, an associate editor for a scientific journal, told the author that this paper has often been referred to in referee reports for papers reporting photocatalytic systems including MB or other dyes. Watanabe et al. have reported a similar action spectrum analysis of photoinduced degradation of Rhodamine B with a cadmium sulfide suspension and pointed out a similar dye-sensitization mechanism: T. Watanabe, T. Takizawa, K. Honda, *J. Phys. Chem.* **1977**, *81*, 1845. Photocatalytic reaction of MB in aerated titania suspensions was reported in 1937 by a Japanese photochemist: M. Horio, *Nihon Gakujutsu Kyokai Hokoku* **1937**, *12*, 204. As far as the author knows, this is the first report on titania photocatalysis.

25 Sometimes the term "active site" is used for a photocatalytic reaction system with dispersed chemical species, e.g., metal complexes or atomically adsorbed species, on support materials. Even in this case, a photocatalytic reaction occurs only when the species absorb light, and species not irradiated therefore cannot be active sites.

26 Photoexcited electrons and positive holes must react with the substrate independently. However, to simplify the discussion, it is presumed here that an electron–hole pair reacts with the substrate.

27 In a recent paper of a collaboration work with the author, discussion of the ratio k_{red}/k_r is presented: S. Murakami, H. Kominami, Y. Kera, S. Ikeda, H. Noguchi, K. Uosaki, B. Ohtani, *Res. Chem. Intermed.* **2007**, *33*, 285.

28 The author thinks that the use of "rate-determining step" for photoreactions is misleading, since a photoreaction in principle proceeds via species in their excited state and they undergo both chemical reaction and deactivation (deexcitation). The assumption for rate-determining step is that the reaction proceeds sequentially, not in parallel, such as photoreactions.

29 The author could not find the original description of why this linear adsorption isotherm is called "Henry-type." One possible reason is the resemblance of linear relation with that of dissolution of gas in liquid.

30 Honestly speaking, the author does not like to describe such criticisms in this article, since some of them have been employed when referee reports were prepared for papers in this field of photocatalysis and thereby authors submitting such papers may recognize that the papers had been rejected by the author's criticism when reading this article. However, the author would like to say that those criticisms may be acceptable for researchers in this field and hence reviewers other than the present author may state them in their reviewers' reports.

31 In this sense, conversely, statistical analyses of the reaction rate with measured properties of photocatalysts may be helpful for estimation of the significance of property on the reaction rate. O. O. Prieto-Mahaney, R. Abe, F. Amano, B. Ohtani, to be submitted.

32 Since the discovery of this phenomenon in 1997 (R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature* **1997**, *388*, 431), it has been believed that this is induced by band-gap excitation of photocatalytic coatings. However, the corresponding action spectra were reported for the first time in 2007 by the author's group (X. Yan, R. Abe, T. Ohno,

M. Toyofuku, B. Ohtani, *Thin Solid Films* **2007**, in press. DOI: 10.1016/j.tsf.2007.10.033).

33 Another frequently asked question is the comparison of photocatalytic activity of brookite. The author used to answer as "Brookite is similar to anatase.", but this tended to be misunderstood as brookite shows better activity than that of rutile as has been observed for anatase. Therefore, it is necessary to state that such comparison does not make sense before answering so. The fact that brookite crystallites were prepared as a mixture with other polymorphs, anatase and/or rutile makes it difficult to discuss their photocatalytic activities, but, even if pure brookite crystallites are obtained, such discussion on the structure is complicated as described in *Structure—photocatalytic activity correlation*.

34 American Chemical Society, *The ACS Style Guide – Effective Communication of Scientific Information*, 3rd ed., ed. by A. M. Coghill, L. R. Garson, Oxford University Press, Oxford, **2006**, 23. This book is recommended by the author to graduate students and postdoctoral fellows, who will write scientific papers in English, and a copy of the book is given to them as a remembrance when they leave the author's laboratory.