Preface

The photocatalysts can decompose stains with the aid of photo energy and have been recognized as being useful for environmental clean-up. They have become rapidly widespread worldwide. The technique was originally developed in Japan with the use of the semiconductor of titanium dioxide aiming at the production of hydrogen by water decomposition. Numerous researches on this subject have begun so far. Several thousand scientific reports on photocatalysts are currently published every year, and it would be almost impossible to look over all of them. However, the proper selection of the necessary issues from this enormous amount of literature would be relatively feasible owing to the development of information systems. However, problems arise over whether the authors correctly refer to the past researches when interesting and relevant reports are found. For instance, almost the same research as Fujishima *et al*. reported in 1975 was published in a prestigious journal, *Science*, 25 years later. In the meantime, four comments that pointed out the mistake in judging the acceptance of the reports were published in *Science* as well (A. Fujishima, *Science*, 2003, **301**, 1673). Among the literature in the field of photocatalysts, a lot of reports whose results were not reproducible even when any researcher studied confirmatory were published in the prestigious journals. One of the reasons why such incorrect papers appear is that the science which it is based on includes many varied fields from physics to chemistry or biology. Photocatalysts are somewhat different from general catalysts, especially because it is currently recognized that the photocatalytic reactions have been developed as the extension of electrode reactions. Therefore, although they are a kind of catalyst, the standpoints are

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often different depending on the research bases. The researches related to photocatalysts cover the research fields such as photochemistry, electrochemistry, catalyst chemistry, radiation chemistry, physical chemistry, organic reaction chemistry, solid-state physics, film science, ceramics science, materials science, *etc*. This book deals with photocatalysis, where generally speaking the photocatalysis is the heterogeneous photocatalysis using semiconductors. As for homogeneous photocatalysis, it belongs to the field of traditional photochemistry, and distinguished textbooks explaining from this basis are available.

Although enormous amounts of research papers on photocatalysts have been published, few introductory textbooks from the scientific viewpoints are presented so far because the field of photocatalysis covers various fields of science as stated above. Therefore, an introductory textbook aiming at understanding the foundation of photocatalysis is indispensable. To introduce scientific bases of photocatalysis to graduate students, no proper textbook seems available, although many specialized books have been published. We have published a book named ''*Introduction to Photocatalysis*'' written in Japanese from Tokyo Tosho, Inc. in 2004. Because a lot of new reports were later published, we felt the necessity of a drastic revision of the book. Meanwhile, the RSC asked us to write a textbook on photocatalysis. Thus, we were willing to publish this book. The object of this book is providing the students and researchers from the faculty of engineering not with novel reviews but mainly with the science. This science will become the base of photocatalysis and provide the way of thinking that makes it easy to understand the concepts towards the practical application of photocatalysts as functional materials.

The number of reports on photocatalysis is still growing. Thus, targeting the subjects in a diversified field, we referred to many books and specialized journals. Our concern is that some reports contradictory to those referred to in this book might appear, which might cause misunderstanding. We would appreciate it if readers could respond positively and give us their honest opinions.

We are grateful to Mr. Masahide Mase of Gijutsu-kyouiku-shuppan (Photo Functionalized Materials Society, PFMS) for promoting to publish the previous Japanese textbook on photocatalysis, and Mr. Tomoyoshi Matsunaga of Tokyo Tosho for approving to use the figures and the illustrations.

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Preface

Contents

Acronyms and Symbols

Chapter 1. What is Photocatalyst?

(Abstract)

This chapter begins with the introduction of the essential factors for practical functional materials. TiO_2 has been mainly used as pigment for a long time and is now highlighted and uniquely used as a practical photocatalyst. The manufacturing process and the history of TiO_2 developments are briefly reviewed. Then it is reviewed in terms of the characteristics and crystal structures and compared to those for the other popular photocatalyst of ZnO. Finally, the history in the field of science and

engineering related to photocatalysis is briefly reviewed starting from the light illumination effect on electrodes of various materials to the recent developments in solar cell.

Chapter 2. Principles of Light over Solids

(Abstract)

Properties of light such as absorption, reflection, interference, and refraction, are surveyed briefly for the essential understanding of the experiments and beneficial applications of photocatalysis. Conventional procedures to calculate the photon energy and the number of photons are introduced. The relationship between optical constants and electric constants is also described along with the concept of electromagnetic wave. In addition, the relation of the colors of materials to the light source is briefly described.

Chapter 3. Principles of Semiconductor

(Abstract)

Electronic structures of semiconductors are briefly described based on the correlation of chemical bonds with the band structures. The concept of band is introduced from the view point of the bunch of electronic energy levels which are increased with increasing the number of the atoms constructing semiconductors. The position of Fermi energy level in the bands and the excitation between bands in the electronic structure are introduced to describe n-type semiconductors. Band gap energy and band edge position are presented for some semiconductors familiar in the reports of photocatalysis. Finally, the size quantization effects for TiO_2 and ZnO are discussed.

Chapter 4. Principles of Photoelectrochemistry

(Abstract)

In this chapter, theories essential for electrochemistry and photoelectrochemistry are described. Starting with three superior characteristics of electrochemical reactions, the surface structure and surface reactions for water electrolysis and hydrogen fuel cell, and the concept of redox potential are presented. Historically important photoelectrochemistry with TiO_2 single crystal electrodes is explained along with the concept of flat band potential and space charge layer. This concept of photoelectrochemistry is extended to particulate semiconductor. Finally, photoelectrode with dye sensitizer is briefly described in terms of the application to solar cells.

Chapter 5. Photocatalyst Surface and Active Species

(Abstract)

In this chapter the surface structure of photocatalysts and the primarily generated unstable species are presented as a previous stage of the detailed description of photocatalytic reactions in the next Chapter. At first it is demonstrated that the surface of metal oxides represented by TiO_2 varies depending on the surrounding situations such as adsorption of water and organic molecules. The electrons and holes which are photogenerated in photocatalysts to be trapped on the surface are described. Then, the active oxygen species, such as OH radical, superoxide radical, singlet oxygen, and hydrogen peroxide, which are produced in the photocatalytic reactions are described from the viewpoints of environmental cleaning.

Chapter 6. Kinetics and Mechanism in Photocatalysis

(Abstract)

Time scale and kinetic analysis of photocatalysis are described to understand the factors to

determine reaction efficiency. Using a simple kinetic model for photoinduced electron - hole pairs, the yield of the initial oxidation or reduction products is mathematically formulated. The effects of light intensity and the substrate concentration on the reaction rates of the photocatalysis are discussed. The proposed reaction mechanisms including the contribution of OH radicals are demonstrated. Then, decomposition of organic compounds for several representative materials is reviewed. In addition, the other reactants, extinction of bacteria, oxidation of water and the surface superhydrophilicity are described. Lastly, dye sensitized mechanism in photocatalysis is presented and the unconscious process in photocatalyst is pointed out.

Chapter 7. Methods for Improving the Photocatalytic Activity

(Abstract)
The recent researches aiming at enhancing a higher photocatalytic activity and the visible light responsibility are surveyed. Various factors affecting the photocatalytic activities such as particle size, crystalline phases and facets, metal ion and anion doping in semiconductors are explained in detail. Furthermore, novel attempts such as surface modifications with fluoride or phosphate treatment, the deposition of transition metal ions or noble metals, the combined use of semiconductors or adsorbents, and the additives in solution are briefly introduced. Finally, the effects of the technical treatments by such as ultrasonic wave, microwave, and magnetic field on the photocatalytic reactions are described.

Chapter 8. Fabrication of Practical Photocatalysts

To utilize photocatalysts such as TiO_2 for practical use, they must be deposited on the substrate, namely they must be immobilized on the surface. For immobilization, the wet process, by which the raw materials of TiO_2 are painted on the surface and then sintered, has been conventionally the major process. However, the dry processes without use of solution such as spattering methods recently have been practically adopted. The immobilization became also possible even for non-heat-resistant materials which cannot be treated at high temperatures. Various coating materials suitable for the immobilization have been developed. In this chapter, the practically utilized photocatalytic materials which are prepared with those immobilization techniques are described.

Chapter 9. Evaluation Methods of Reactivity

Evaluation methods of photocatalysts proposed by ISO will be mainly described. Firstly, the ultraviolet and white fluorescent lamps used for the evaluation are summarized. Next, the evaluation tests of the self-cleaning performance of photocatalyst products, namely the decomposition test of methylene blue and the test with which the decomposition of the adsorbed organic compound is measured by the contact angle with the water are introduced. Then, as for the evaluation of the performance of air-purification, the removal performances of pollutants, such as nitric oxide, acetaldehyde, toluene, formaldehyde, and methylmercaptane, will be described. Among them, the removal test of formaldehyde in a small-test chamber will be introduced. Because novel materials are often fabricated as powders, the evaluation methods for powders are required. Thus, a complete decomposition method of acetaldehyde, and the evaluation method of photocatalytic activity by the consumption of dissolved oxygen are introduced. For water purification, the decomposition of DMSO was used in ISO test. The novel evaluation methods of disinfection performance of photocatalyst targeting bacteria, fungi, virus, and algae are described. Finally, as for the decomposition of water to provide hydrogen energy which is not adopted by ISO, an evaluation method is introduced.

Chapter 10. Future Applications of Photocatalysis

Among the functions of photocatalysts, air cleaning, antifouling, antifogging, and antibacterial functions are practically applied today, and further applications for various fields are additionally expected in the future. Taking account of the global environmental problems nowadays, the decomposition of water to hydrogen and oxygen to utilize hydrogen gas energy would be a high research goal. The reduction of carbon dioxide with photocatalysts are also expected. Besides, in this chapter the topics which are applied and developed in the various industrial fields by using the characteristics of photocatalysts, such as sensor, medical treatments, organic synthesis reactions, agriculture waste fluid processing , sterilization treatment of sea water, printing , cooling of the outer walls of building by use of the superhydrophilicity etc. will be taken up.