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Invited review

Photoelectrochemical properties of TiO_2 photocatalyst and its applications for environmental purification

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ABSTRACT

In view of the situation that environmental issues become more serious day by day, recent studies on practical applications of TiO_2 photocatalysis for environmental purification are reviewed. Although the fundamental aspects and the mechanisms of TiO_2 photocatalysis have recently become quite well understood, effective photocatalytic environmental purifier, especially water purifier, could not be developed to the stage of real industrial technology. The removal rate of gaseous or aqueous contaminants is influenced by numerous parameters; UV light intensity, substrate concentration, O_2 partial pressure, humidity, substrate type, and so on. Moreover, TiO_2 photocatalyst essentially has a difficulty in decomposition of large amount of contaminants or refractory chemicals. As the solutions of these problems, combination with other processes such as advanced oxidation processes and improvement of the design of photocatalytic environmental purification systems are described. During the past several years, the strategies for effective design of the system are well discussed and evaluated. The reactor design for air- or water-purification can be classified into two main strategies: (1) enlargement of reactive surface area and (2) improvement of mass transfer. Based on these insights, very recent achievements for development of photocatalytic environmental purification system with our contribution in each aspect and future research directions are reviewed.

Contents

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Tsuyoshi Ochiai was born on 1979, in Nagoya, Aichi Prefecture, Japan. He completed a doctoral course at the Nagoya Institute of Technology Graduate School of Engineering, Department of Materials Science and Engineering and gained a Ph.D. in engineering in 2008. From April 2005 to March 2008, he worked for the Central Japan Railway Company as a research engineer in the Functional Materials Team, Technical Research and Development Department, General Technology Division. He has been a full-time researcher in the Photocatalyst Group at the Kanagawa Academy of Science and Technology since April 2008. Since April 2010, he has also been a part-time lecturer (chemistry) at the Nippon Institute of Technology. Since January 2011, he has also been a visiting researcher of Tokyo University of Science. His research interests involve photosynthesis, photoelectrochemistry, and environmental chemistry.

Akira Fujishima was born in 1942 in Tokyo. He received his Ph.D. in Applied Chemistry at the University of Tokyo in 1971. He taught at Kanagawa University for four years and then moved to the University of Tokyo, where he became a Professor in 1986. In 2003, he retired from this position and took on the position of Chairman at the Kanagawa Academy of Science and Technology. From 1st of January 2010, he became President of Tokyo University of Science. His main interests are in photocatalysis, photoelectrochemistry, and diamond electrochemistry. He served as the President of various scientific societies, the Japanese Association of Photochemistry, the Electrochemical Society of Japan, and the Chemical Society of Japan. He has received many awards for his research excellence from various societies, such as the Electrochemical Society of Japan, the Chemical Society of Japan, and the Federation of Asian Chemical Societies. In 2004, he has been awarded the Japan Academy Prize and the Japan Prize for Science. He has been designated as a Person of Cultural Merit 2010. In 2011, he has also been awarded the Luigi Galvani Medal.

1. Introduction

Environmental purification is one of the most important technologies for human life. Application of the strong oxidation ability of photo-excited TiO_2 for environmental purification has received growing attention. In 2008, one of the present authors (AF) summarized TiO_2 photocatalysis and related surface phenomena with its historical overview, fundamentals of photocatalysis and photo-induced hydrophilic effect, and brief review of its applications, as a review article [1]. Now the review article had become one of the most cited papers in chemistry, on the other hand, environmental issues become more serious day by day. Therefore, we feel urgency of publication of another review article which focused on recent practical applications of TiO_2 photocatalyst for environmental purification systems, especially indoor air purifier and polluted water purifier.

This review summarizes very recent studies with theoretical strategies for effective design of the systems based on fundamentals of TiO_2 photocatalysis. Our recent contribution in each aspect and future research directions are also mentioned.

2. Background

2.1. Historical overview

In the late 1960s, one of the present authors (AF) began to investigate the photoelectrolysis of water, using a single crystal TiO_2 electrode. Then, the first report on the efficient hydrogen production from water by TiO_2 photocatalysis was published in Nature in 1972, at the time of "the oil crisis" [2]. Thus, TiO_2 photocatalysis drew the attention of many people as one of the promising methods to obtain the new energy source. However, although having a large surface area-to-volume ratio, the aqueous suspension of TiO_2 powder shows very low reaction efficiency for H_2 production. Kawai and Sakata concluded that the produced H_2 and O_2 gases might recombine to regenerate H_2O through the back reaction in the powder system, because the production sites of H_2 and O_2 gases are located close to each other [3]. Moreover, TiO_2 can absorb only the UV light contained in a solar light, which is only about 3%. Therefore, from the viewpoint of H_2 production technology, TiO_2 photocatalysis is not very attractive. Recently, photocatalytic water splitting and H_2 evolution are studying by using not only TiO_2 but also many kinds of novel photocatalyst materials. Kudo and Miseki surveyed heterogeneous photocatalyst materials for water splitting [4]. They have concluded that the target for efficiency for water splitting is 30% in terms of a quantum yield at 600 nm. This efficiency gives about 5% of solar energy conversion. The $Cr_xRh_{2-x}O_3$/GaN:ZnO and Ru/$SrTiO_3$:Rh-$BiVO_4$ photocatalysts respond to about 500 nm for overall water splitting so approaching the target but the quantum yield is still low. Therefore, the photocatalytic water splitting is still a challenging reaction even if the research history is long. On the other hand, Frank and Bard showed the decomposition of cyanide in the presence of aqueous TiO_2 suspensions [5]. After this report, the research shifted to the utilization of the strong photoproduced oxidation power of TiO_2 for the decomposition of various contaminants in both water and air in the 1980s. At the same time, the immobilization of TiO_2 powders on supports was carried out for the purpose of easy handling of photocatalysts. Then, the novel concept of light-cleaning materials coated with a TiO_2 film photocatalyst under UV light was investigated. In 1997, the marked change in the water wettability of the TiO_2 surface before and after UV light irradiation was also reported in *Nature* as a novel phenomenon of TiO_2 photocatalysis [6]. With the discovery of this phenomenon, now the application range of TiO_2 coating has been largely widen, as mentioned in Fig. 1 and the literatures [1,7–14].

2.2. Papers, patents, and market transition related to photocatalysis

Paz presented a review of papers and patents on the application of TiO_2 photocatalysis for environmental purification in 2010 [15]. Fig. 2a and b show the estimated number of scientific manuscripts and new patents on TiO_2 photocatalysis per year, categorized according to: water treatment, air treatment, and self-cleaning surfaces. Paz analyzed this trend that the years 1995–2000 seem to be the "booming" years in which the annual number of papers and