



Advances of Photocatalysis Science & Engineering for TiO₂-Based Photocatalysts: Environmental Pollutants Controlling

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Resume of editor-in-chief



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Foreword

The past 40 years have seen the emergence worldwide of a growing desire to take positive actions to restore and protect our environment from the degrading effects of all forms of pollution. Since this pollution is a direct or indirect consequence of waste, the seemingly idealistic demand for “zero discharge” can be construed as an unrealistic demand for zero waste. However, as long as waste exists, we can only attempt to abate the subsequent pollution by converting it to a less noxious form. In recent years, the international environment community, especially in China, has been increasingly concerned about the stresses imposed on the natural environment by many chemical and energy-generating processes. As a result, the whole world is witnessing an accelerated development and implementation of new green technologies which are called to provide ecologically responsible solutions for the much needed supply of drinking water and clean air.

Photocatalysis, hold great promise for delivering these ground-breaking technologies, is a truly environmentally friendly process where irradiation, either near UV or solar light, and promotes photoexcitation of semiconductor solid surfaces. As a result, mobile electrons and positive surface charges are generated. These excited sites and electrons accelerate oxidation and reduction reactions, which are essential steps for pollutant degradation. Photocatalysis and its related technological issues have been strongly influenced by recent publications.

The treatment of the various engineering and science presented in “Advances of Photocatalysis Science & Engineering for TiO_2 -Based Photocatalysts” will show how a process concerned their formulation of the subject flows naturally from the fundamental principles and theory of chemistry, physics, and mathematics. This emphasis on fundamental science recognizes that engineering practice has in recent years become more firmly based on scientific principles rather than its earlier dependency on the empirical accumulation of facts. The present book aims at offering a comprehensive overview of the state-of-the-art photocatalytic science and technology. It will be seen in this book of the fundamentals and selected applications of photocatalysis, principally on titanium dioxide based photocatalyst, that there is a host of reports concerned the waste water and gaseous pollutants treatment. The work will be divided into several sections as follows.

Part I. Progress of Photocatalysis Science and Technology. In this chapter, the developing history of photocatalysis, photocatalysts, and photocatalytic reactor designs for application in degradation of gaseous and aqueous pollutants to achieve increased the photocatalytic conversion performance were reviewed.

Part II. Fundamentals of photocatalysis. Fundamentals of TiO_2 -based photocatalysts were reviewed, including the photocatalysis mechanism, the behaviors of charge carriers after their creation, various electron transfer processes at TiO_2 surfaces, and the electron transfer and catalytic aspects of TiO_2 photocatalysis.

Part III. Heterogeneous photocatalytic degradation of waste water containing phenol/ phenolic compounds. In this section, we summarized and highlighted the decomposition mechanisms and special operating parameters on the photocatalytic degradation of phenols and its derivatives in waste water together with recent reports. Then, the recent researches on the modified TiO_2 -based photocatalysis under visible and/or solar light were reviewed to improve the photocatalytic degradation efficiency of phenol/phenolic compounds in waste water by means of metal, non-metal and ion doped. The existing limitation and future research needs associated with the treatment technology pertaining to the contaminant of interest are also discussed.

Part IV. Heterogeneous photocatalytic degradation of waste water containing dyes. The main aim of this part is to produce a condensed and coherent overview on the photocatalytic degradation mechanisms, pathways, influencing factors, and controlling processes of dyes in the presence of TiO_2 -based photocatalysts, which can serve as a ready reference for future scientific endeavors in this area.

Part V. Heterogeneous photocatalytic removal of inorganic ions from waste water. Here, we will summarize ① the performance of TiO_2 -catalyzed photocatalytic oxidation (PCO) and adsorption of As(III) and Cr(III) by various TiO_2 -based photocatalyst; ② the methods to improve removal efficiency; ③ the influence of co-existing solutes on removal efficiency; ④ the mechanisms of As(III) and Cr(III) photocatalytic oxidation by TiO_2 -based photocatalytic reaction and adsorption on TiO_2 .

Part VI. Heterogeneous photocatalytic degradation of gaseous pollutants. We will present updated progress concerning photocatalytic degradation mechanism and intermediates in this area, discussed the influencing factors in photocatalysis at various experimental environments, and summarized various catalyst systems for photocatalysis under UV and visible light. The important factors that influence the catalytic activity and the kinetics will be discussed. The future research directions will also be presented.

Part VII. References.

In sum, this book contains an up-to-date discussion of photocatalysis fundamentals and their applications in the treatment of waste water and gas pollutants. Altogether it is an invitation to reflect on the possibilities of photocatalysis as a new and unique technique with great potential for air and water treatment. We offer our book as a contribution to the development of photocatalytic reaction science and engineering as well as to the extensive potential for application of this technology.

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1 Progress of Photocatalysis Science and Technology

Introduction

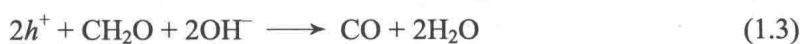
In chemistry, photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity depends on the ability of the catalyst to create electron-hole pairs, which generate free radicals (e.g. hydroxyl radicals, $\cdot\text{OH}$) when undergoing secondary reactions. Its practical application was made possible by the discovery of water electrolysis by means of titanium dioxide. The commercially used process is called the advanced oxidation process (AOP). There are several ways the AOP can be carried out, which maybe (but do not necessarily) involve TiO_2 or even the use of UV light. Generally the defining factor is the production and use of the hydroxyl radical. If you like some aspects of photocatalysis science & engineering, you should acquire the development history of this subject. Here, just as reviewed by Fujishima et al., a brief overview of the early history of photocatalysis will be given based on papers that we have been able to access, which means that we may be ignoring some important papers.

1.1 A brief overview of photocatalysis

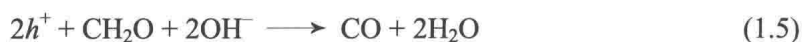
The earliest work to be found is the result of Renz, at the University of Lugano (Switzerland), who reported in 1921 that titanium dioxide is partially reduced during illumination with sunlight in presence of an organic compound such as glycerol, the oxide turning from white to a dark color, such as gray, blue or even black. In addition, he found similar phenomena with CeO_2 , Nb_2O_5 and Ta_2O_5 . For TiO_2 , the reaction was proposed as:



Baur and Perret, at the Swiss Federal Institute of Technology, were the first to report that the photocatalytic deposition of a silver salt on zinc oxide to produce metallic silver. Evenly, the authors suspected that both oxidation and reduction were occurring simultaneously. The reaction pathway proposed was:



Three years later, Baur and Neuweiler proposed simultaneous oxidation and reduction to explain the production of hydrogen peroxide on zinc oxide.



However, Renz reported the photocatalytic reduction of silver nitrate to metallic silver and gold chloride to metallic gold on a number of illuminated oxides in 1932, including TiO_2 and Nb_2O_5 , and discussed the results according to the Baur redox mechanism. It has been recognized for quite a long time that titania-based exterior paints tend to undergo “chalking” in strong sunlight. This effect was recognized as a result from the actual removal of part of the organic component of the paint, leaving the titania itself exposed.

Goodeve and Kitchener, at University College in London, carried out an excellent study on the photocatalytic decomposition of a dye on titania powder in air in 1938, including absorption spectra and determination of quantum yields (Fig. 1.1). They proposed that titania acts as a catalyst to accelerate the photochemical oxidation, combined with the investigation into a number of other oxides, and then speculated on the precise mechanism Goodeve and Kitchener.

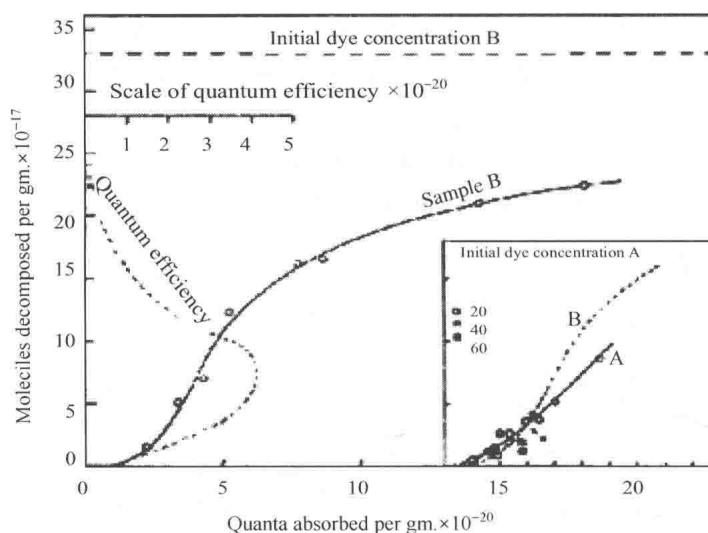


Fig. 1.1 Original data of Goodeve and Kitchener showing the photocatalytic decomposition of a dye (“chlorazol sky blue”) adsorbed on anatase powder under UV illumination at wavelength of 365 nm

Jacobsen, at the National Lead Company (USA), attempted to explain the paint chalking phenomenon in terms of a redox mechanism. He found a correlation between the tendency of a number of different titania powders to undergo photo-induced reduction in the presence of organic compounds to their chalking tendency. The photo-induced reduction was measured as a loss of reflectivity, due to the discoloration of the powder upon reduction, presumably to various oxygen-deficient forms, all the way to Ti_2O_3 . The author proposed a cyclic redox process in which the titania was reduced while the organic paint components were oxidized, followed by re-oxidation of the titania by oxygen from the air. The changes experienced by the titania were recognized to be completely reversible, while those experienced by the organic paint were recognized to be irreversible, leading to the formation of water-soluble organic acids and CO_2 . Even though he was apparently unaware of the work of Baur on the redox mechanism, he referred to the result of Renz

on the photo-reduction of metal oxides and proposed the same basic mechanism that had been proposed by Baur; thus, a foundation was laid for later work on the redox mechanism.

During the 1950s, the development of photocatalysis shifted to zinc oxide. In 1953, two works appeared in which the puzzling phenomenon of hydrogen peroxide production on zinc oxide illuminated with UV light was studied, followed by a series of follow-up studies in ensuing years. In these works, the overall reactions and mechanisms were completely clarified, and it became apparent that an organic compound was oxidized while atmospheric oxygen was reduced. Even in the earliest study, an overall reaction with phenol to produce catechol was proposed, and the involvement of radical species such as the hydroxyl radical was also speculated upon. Thus, the original proposal of Baur and Neuweiler was finally confirmed, with the overall reaction:



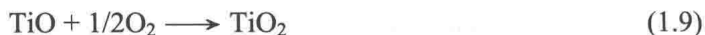
Markham et al., first at the Catholic University of America and later at St. Joseph's College (USA), continued to study photocatalytic reactions on ZnO, and her papers constitute an impressive, yet underappreciated, body of work. This work culminated in a highly intriguing study in which Markham and Upreti constructed and studied a number of different types of photo-assisted fuel cells, using illuminated ZnO as the photo-anode with formamide or several alcohols as the organic substrates. At the dark cathode (platinum), several different redox mediators were examined, with atmospheric oxygen ultimately being the electron acceptor. They may have been discouraged by the inevitable problem of ZnO photocorrosion, which prevented this system from reaching practical application. After years later, the same basic ideas were re-examined with TiO₂. Unfortunately, Markham and Laidler, in their initial study, examined TiO₂ but subsequently abandoned it, since it did not produce measurable amounts of hydrogen peroxide.

It should be interesting to note that Stephens et al., worked in Wayne State University, in their study of hydrogen peroxide production on a large assortment of illuminated semiconductors, but, unfortunately, not TiO₂, remarked that "zinc oxide and the other catalytic solids should not be abandoned as devices for capturing solar energy in a form capable of transfer to some chemical system". They observed that CdS was the most active photocatalyst, exceeding the activity of ZnO.

As reported in 1956 in *Nature*, Hindson and Kelly (Defense Standards Laboratory) reported on the effects of various rot-inhibitors on tent fabrics for use in Australia. They examined the effects of fabric strength after one year of exposure to sunlight. They stated: "the effect of anatase is startling. Fabrics containing 3% of this pigment lost 90% in strength".

To 1958, Kennedy et al., at the University of Edinburgh, studied the photo-adsorption of O₂ on TiO₂ in order to understand the photocatalytic process completely. They concluded that electrons were transferred to O₂ as a result of photoexcitation, and the resulting reduced form of O₂ adsorbed on the TiO₂ surface, eventually, found that a correlation between the ability of the TiO₂ sample to photocatalytically decompose chlorazol sky blue (the same dye used earlier by Goodeve and Kitchener) and the ability to photo-adsorb O₂. This phenomenon is certainly important for photocatalysis and will be commented upon later.

During this period, researchers in Russia were active. Photo-adsorption of O_2 on illuminated ZnO was studied by Terenin and Solonitzin at the University of Leningrad (now University of St. Petersburg). In a very interesting early work, Filimonov, at the same institution, compared the photocatalytic oxidation of isopropanol to acetone on ZnO and TiO_2 and concluded that the mechanism on TiO_2 involved an overall reduction of O_2 to H_2O_2 , while the reduction of O_2 on ZnO only went as far as H_2O_2 . On TiO_2 , the surface reactions were proposed to be:



Thus, this mechanism is a more detailed version of the Gaur cyclic mechanism. It involves the removal of a surface lattice oxygen atom, which would be a kind of reduction process.

In Japan, at the Kyoto Institute of Technology, an early study by Kato and Mashio also found that various types of titania powders had different photocatalytic activities, specifically to oxidize hydrocarbons and alcohols, simultaneously producing hydrogen peroxide. Interestingly, they found that anatase powders were more active than the rutile ones.

The further work at the University of Edinburgh, carried out by McLintock and Ritchie using gas-phase adsorption measurements, studied the photocatalytic oxidation of ethylene and propylene at TiO_2 . This work is one of the first that we have found that shows that it is possible to oxidize organic compounds completely to CO_2 and H_2O :



The mechanism was proposed to involve the production of superoxide from oxygen:



Markham et al. had already proposed this reaction to take place on illuminated ZnO. Work on similar photo-reactions has continued into more recent years. In an important study for the relationship between photoelectrochemistry and photocatalysis, Lohmann and Bunsenge at the Cyanamid European Research Institute, in 1966 published a highly detailed study of the photoelectrochemical (PEC) behavior of ZnO, both in the presence and absence of redox couples, including ferro/ferricyanide and methylene blue. He clearly showed that the overall current at the ZnO electrode under illumination is the sum of anodic and cathodic currents, the anodic current being a combination of the dissolution of the ZnO itself and the oxidation of any redox species present. The cathodic process was the reduction of O_2 to H_2O_2 . This same approach had been introduced in 1938 by Wagner and Traud, at the Technical University of Darmstadt, to help explain the corrosion of metals, coupled with either hydrogen evolution or oxygen reduction.

Another PEC study, Morrison and Freund, at the Stanford Research Institute, studied the photocatalysis of ZnO. They demonstrated in detail the various situations that arise in the presence and absence of redox couples. They also showed that oxidation products of some organic compounds are different in the case of the PEC electrode poised at the open circuit potential, i.e.,

with both oxidation and reduction currents balanced, compared to the case of a purely electrochemical oxidation. This difference was proposed to be due to the presence of cathodically generated superoxide, as the key points in understanding photocatalysis.

During the late 1960s, Fujishima et al., at the University of Tokyo, began to study the photoelectrochemistry of titania and found that oxygen gas was evolved at potentials very much shifted from the thermodynamic expectation, for example, with an onset of ca. -0.25 V vs. the standard hydrogen electrode (SHE), compared to the standard potential of $+0.95$ V in pH 4.7 aqueous buffer (Fig. 1.2). At first, there was skepticism of this result, but then it slowly became accepted. One reason that this result was difficult to understand is that the photoexcitation process converts the photon energy to chemical energy with little loss, and thus the photogenerated hole has a very high reactivity, so that it can react directly with either water or quite robust organic and inorganic compounds. Subsequently, a number of studies were carried out in which the photoelectrochemical oxidation process on TiO_2 was examined for the competitive oxidation of water to O_2 with the oxidation of a variety of inorganic and organic substrates. Both types of reactions, of course, involve the use of light energy to get over an energy barrier, either an overall uphill process, as in the case of O_2 evolution, or an overall downhill process, as in the case of organic oxidations.

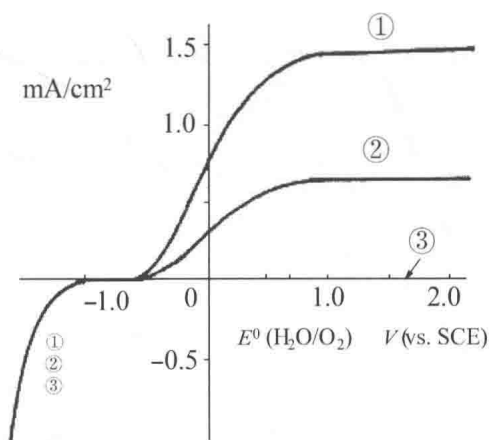


Fig. 1.2 Photocurrent vs. potential for illuminated rutile single crystal. SCE refers to the saturated calomel electrode, which is 0.241 V vs. the standard hydrogen electrode (SHE) and picture of Akira Fujishima (March 10, 1942) is a Japanese chemist, professor emeritus, University of Tokyo, known for significant contributions to the discovery and research of photocatalytic and superhydrophilic properties of titanium dioxide

With Fujishima and Honda's reports of the ability to simultaneously generate hydrogen gas in 1972 (Fig. 1.3), the PEC field started to receive much wider attention, due to its implications for solar energy conversion. From this point, also, photoelectrochemistry became closely associated with photocatalysis.

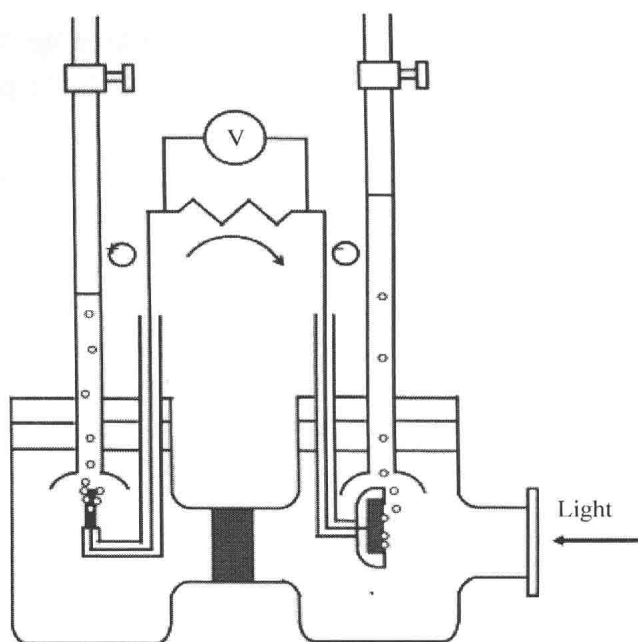


Fig. 1.3 Photoelectrochemical cell used in the photolysis of water

In particular, some of the early work of Bard and co-workers at the University of Texas should be mentioned. Frank and Bard were the first ones to propose that illuminated TiO_2 could be used for the purification of water via the photocatalytic decomposition of pollutants. They suggested that cyanide and sulfite could be photocatalytically oxidized to cyanate and sulfate, respectively. In one of these studies, they found that photocatalytic oxidations could also occur at other illuminated semiconductors, such as ZnO , CdS , Fe_2O_3 and WO_3 . The most active semiconductor was found to be ZnO . These authors expanded this study to a long list of inorganic and organic species and speculated that photocatalysis could be a useful approach to both environmental cleanup and photo-assisted organic synthesis. They also suggested that each small illuminated semiconductor particle could be considered as a PEC cell, with both photo-assisted oxidation and dark reduction reactions taking place. It is important that they proposed photocatalysis as a way to remove toxic metals from wastewater.

In contrast, the developments of photocatalysis in China as described by Zheng et al. also should be mentioned here in brief. There was scarcely any research on photocatalysis before 1975, while after that, photocatalysis research grew exponentially due to the fact as the rapid economic growth of China and the accelerated homecoming trend of Chinese researchers from Japan, America and European countries. Here, the development history of photocatalysis in China will be divided into three periods, 1975~1985, 1985~1995, and 1995~2014. In the 1975~1985 period, intense researchers were achieved on the photocatalytic hydrogen production using metal complexes or semiconductor nanoparticles. It was focused on by some scientific research institutions and universities, including Dalian Institute of Chemical Physics of Chinese Academy of Sciences, Lanzhou Institute of Chemical Physics of Chinese Academy of Sciences, Jilin University, Shandong University, Wuhan University and so on. A major system for photocatalytic hydrogen production by

splitting water was comprised of a photosensitizer, electron mediator, electron donor, surfactant, and other additives.

From 1985 to 1995, especially in the mid-1980s, research on photocatalytic splitting water reached its low point, while the work involved the photocatalytic degradation of environment pollutants and reduction of heavy metal ions were approximated to the peak. In particular, the photo-reduction rate of Cr(VI) heavy metal pollutant was greatly improved with either an artificial light source or with sunlight. The photocatalytic reduction of metal ions provided a new pathway for environmental protection under mild conditions.

The 1995~2014 period highlighted the diversified development of photocatalyst in all its aspects, including new solar energy conversion from carbon dioxide, co-doped photocatalyst, modification technology for the surface of catalyst to overcome their defaults in real applications, relationship between catalyst structure and performance in application, even for mechanism, etc. It was largely attributed to advances in nanotechnology and advanced characterization techniques, i.e. TEM, SEM, EELS, ESR, and XPS. However, for the large scale production of solar fuels as well as getting deep insights on the photocatalyses, more development is still needed that will rely on innovative breakthrough in various research fields, such as material science, surface/interface science, catalysis, electrochemistry, and environment science and technology, thereafter, integrating their knowledge gained into photocatalysis research. Here, fabricating TiO_2 in the form of nanosheets can provide more active sites on the surface and generate unique charge-bearing effects. Anatase TiO_2 nanosheets presented an excellent activity in the photocatalytic decomposition of organic contaminants due to the exposure of highly reactive (001) facets which were stabilized by fluorine ions on the facets. In addition, hierarchical macro/mesoporous titanias can be fabricated by using mixed surfactants or through a simple hydrolysis of tetrabutyltitanate without additives followed by heating. This material was demonstrated to be an interesting photocatalyst for environmental purification. Excellent photocatalytic activity is presented in mesoporous titania materials with a specific morphology, such as sponge-like macro/mesoporous titania, mesoporous titania hollow microsphere, and mesoporous titania nano-rod/tube composites.

Here, what we want to describe the breakthrough of C. Li Group recent years. Approaches to solar water splitting include photocatalytic water splitting with homogeneous or heterogeneous photocatalysts, photoelectrochemical or photoelectro catalytic (PEC) water splitting with a PEC cell, and electrolysis of water with photovoltaic cells coupled to electrocatalysts (Fig. 1.4). Water splitting is a thermodynamically uphill reaction, requiring transfer of multiple electrons, making it one of the most challenging reactions in chemistry. In 2013, Li Can Group published "Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis" in *Accounts of Chemical Research*, reviewed the PEC water splitting reactions. For semiconductor-based photocatalytic and PEC systems, they show that loading proper cocatalysts, especially dual cocatalysts for reduction and oxidation, on semiconductors (as light harvesters) can significantly enhance the activities of photocatalytic and PEC water splitting reactions since ① the cocatalyst can provide trapping sites for the photogenerated charges and promote the charge separation, thus enhancing the quantum efficiency;