Environmentally Benign Photocatalysts
Environmentally Benign Photocatalysts

Applications of Titanium Oxide-based Materials
Preface

Over the past few decades, mankind has observed an unprecedented and remarkable growth in industry, resulting in a more prosperous lifestyle for peoples of many countries. In developing countries, however, explosive industrial growth is just now beginning to raise the living standards of the people. Most industries, especially in these developing countries, are still powered by the burning of fossil fuels; consequently, a lack of clean energy resources has caused environmental pollution on an unprecedented large and global scale. Toxic wastes have been relentlessly released into the air and water leading to serious and devastating environmental and health problems while endangering the planet and life itself with the effects of global warming.

To address these urgent environmental issues, new catalytic and photocatalytic processes as well as open-atmospheric systems are presently being developed that can operate at room temperature while being totally clean and efficient and thus environmentally harmonious. Essential to technologies harnessing the abundant solar energy that reaches the earth are the highly functional photocatalytic processes that can utilize not only UV light, but also visible light.

Titanium oxide-based catalysts are especially promising as some of the most stable, nontoxic, readily available photofunctional materials known today. The successful development of second-generation titanium oxide photocatalysts using an advanced metal ion-implantation technique, which was first reported at the TOCAT-3 international conference in 1998 in Tokyo, led to reactions that could be induced not only with UV light, but also visible light. Since then, efficiency has improved as new materials and synthesis methods have been developed.

Up until the early 1960s, scientists primarily investigated the effect of UV light irradiation of semiconducting catalysts on the rate and selectivity of catalytic surface reactions in connection with the semiconductor electric band theory. Since Honda and Fujishima’s discovery in 1972 of the photosensitizing effect of TiO₂ electrodes on the electrolysis of water using Pt metal and TiO₂ semiconducting electrodes, investigations of the conversion of photon energy into useful chemical energy with photofunctional semiconducting catalysts have gained momentum.
The photocatalytic decomposition of water into H₂ and O₂ using semiconducting catalysts, such as TiO₂ particles, has also been investigated, and there have been many studies focusing on the mechanisms behind the primary processes of photocatalysis in order to prepare and design catalysts with high reactivity and efficiency. The small particle effect, size quantization effect, and high dispersion effect on photocatalysis were identified in the period 1980–1988, leading to the development of photofunctional zeolite catalysts that incorporated various transition metal cations, such as Ti⁴⁺, Mo⁶⁺, V⁵⁺, et al., in their framework structures. Then, in the 1990s, the focus of the investigations shifted to the use of TiO₂ photocatalysts in the decomposition of toxic compounds dissolved in water and air since TiO₂ exhibited a high photocatalytic reactivity for the degradation of organic compounds into CO₂ and H₂O even under weak UV light irradiation from sunlight. In 1995, the photo-induced superhydrophilicity of TiO₂ thin film photocatalysts was observed by Fujishima et al., resulting in the use of TiO₂ thin films in photofunctional materials having self-cleaning and antifogging properties. Thus, not only powdered catalysts, but also thin film catalysts could be utilized in photofunctional materials in applications for creating and sustaining a cleaner and safer environment.

Through the years, we have seen a great evolution not only in catalytic and photocatalytic research, but also in various applications. TiO₂ catalysts are especially promising as some of the most stable, nontoxic, readily available and photofunctional materials known today. Since the development of visible light-sensitive second-generation TiO₂ photocatalysts using advanced ion-engineering techniques, such as metal ion-implantation and RF magnetron sputtering deposition, the challenge now is to engineer more highly efficient and effective TiO₂ photocatalysts that can operate under both UV and solar or visible, natural light.

This book covers the various approaches in the design of efficient titanium oxide-based photocatalysts by such methods as sol-gel, precipitation, dip-coating, metal implantation, and sputtering deposition. It will introduces the most recent advances in TiO₂ research and its potential applications as well as detailed and fundamental characterization studies on the active sites and mechanisms behind the reactions at the molecular level. This book should serve not only as a text for research into photochemistry and photocatalysis, but also to inspire additional applications into environmentally-harmonious technologies.

The editors would like to thank each contributor for his/her valuable efforts not only for their tireless research into the development of efficient photocatalysts, but also for their important role in making this world a better place for all.
Contents

Part I Introduction

1 Introduction ............................................................... 3
M. Anpo and P. Kamat

Part II Synthesis and Characterization Studies
of Highly Active Titanium Oxide-based Photocatalysts

2 Chemical Methods for the Preparation of Multifunctional
Photocatalysts ............................................................. 7
Jinlong Zhang, Ye Cong, and Masakazu Anpo

3 Second Generation Visible-Light-Active Photocatalysts:
Preparation, Optical Properties, and Consequences
of Dopants on the Band Gap Energy of TiO₂ ......................... 35
Nick Serpone, Alexei V. Emeline, Vyacheslav N. Kuznetsov,
and Vladimir K. Ryabchuk

4 Preparation of Titanium Oxide-Based Powders
and Thin Films of High Photocatalytic Activities
Using Solvothermal Methods ............................................ 113
Hiroshi Kominami and Bunsho Ohtani

5 Preparation of Highly Transparent TiO₂-based Thin Film
Photocatalysts by an Ion Engineering Method:
Ionized Cluster Beam Deposition ...................................... 133
Masato Takeuchi and Masakazu Anpo
6 UV Raman Spectroscopic Studies on Titania: Phase Transformation and Significance of Surface Phase in Photocatalysis .................................................. 153
Jing Zhang, Qian Xu, Zhaochi Feng, and Can Li

7 Photoluminescence Spectroscopic Studies on TiO$_2$ Photocatalyst ................................................. 185
Jianying Shi, Xiuli Wang, Zhaochi Feng, Tao Chen
Jun Chen, and Can Li

8 Surface Chemistry of TiO$_2$ Photocatalysis and LIF Detection of OH Radicals ........................................ 205
Yoshio Nosaka

9 Local Structures, Excited States, and Photocatalytic Reactivities of “Single-Site” Ti-Oxide Photocatalysts Constructed Within Zeolites or Mesoporous Materials .............. 217
Masaya Matsuoka and Masakazu Anpo

Part III Development of Visible Light-Responsive Titanium Oxide Photocatalysts

10 Visible-Light-Responsive Titanium Dioxide Photocatalysts .......... 235
Jinkai Zhou and X.S. Zhao

11 Development and Sensitization of N- or S-Doped TiO$_2$ Photocatalysts .................................................. 253
Teruhisa Ohno and Toshiki Tsubota

12 Visible Light-Responsive Titanium Oxide Photocatalysts: Preparations Based on Chemical Methods .................. 277
Marcos Fernández-García, Arturo Martínez-Arias, and José C. Conesa

13 Development of Well-Defined Visible Light-Responsive TiO$_2$ Thin Film Photocatalysts by Applying a RF-Magnetron Sputtering Deposition Method .......................... 301
Masato Takeuchi and Masakazu Anpo
### Part IV Photocatalytic Reactions for Environmentally-Harmonious Applications

14 **Photo-assisted Mineralization of the Agrochemical Pesticides Oxamyl and Methomyl and the Herbicides Diphenamid and Asulam**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hisao Hidaka, Teruo Kurihara, and Nick Serpone</td>
<td>321</td>
</tr>
</tbody>
</table>

15 **Purification of Toxic Compounds in Water and Treatment of Polymeric Materials**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho-In Lee, Jae-Hyun Kim, Han-Su Lee, and Weon-Doo Lee</td>
<td>345</td>
</tr>
</tbody>
</table>

16 **Development of Highly Active Titanium Oxide Photocatalysts Anchored on Silica Sheets and their Applications for Air Purification Systems**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Takeshi Kudo, Yuko Kudo, Akira Hasegawa, and Masakazu Anpo</td>
<td>403</td>
</tr>
</tbody>
</table>

17 **Photocatalytic Application of TiO₂ for Air Cleaning**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yong-Gun Shul, Hak-Soo Kim, Hyun-Jong Kim, and Myung-Keun Han</td>
<td>415</td>
</tr>
</tbody>
</table>

18 **Photocatalytic Removal of Gas-Phase Elemental Mercury Using TiO₂**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tai Gyu “Teddy” Lee</td>
<td>437</td>
</tr>
</tbody>
</table>

19 **Photocatalytic Purification of Benzene in Air**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xinchen Wang and Xianzhi Fu</td>
<td>451</td>
</tr>
</tbody>
</table>

20 **The Effect of Addition of Pt on the Gas Phase Photocatalysis over TiO₂**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deniz Uner</td>
<td>479</td>
</tr>
</tbody>
</table>

21 **Photoreactions of Organic Compounds with TiO₂ Single Crystal Surfaces**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hicham Idriss</td>
<td>503</td>
</tr>
</tbody>
</table>
Part V  Photo-Induced Superhydrophilicity for Materials with Self-Cleaning Properties

22  Investigations of the Photoinduced Superhydrophilicity of the TiO$_2$ Photocatalyst Surface by Near-Infrared Spectroscopy .............................................................. 527
Masato Takeuchi, Gianmario Martra, Salvatore Coluccia, and Masakazu Anpo

Part VI  Photocatalytic Water-splitting for the Evolution of H$_2$ from H$_2$O

23  Photocatalytic Hydrogen Production from Water on Visible Light-Responsive TiO$_2$ Thin Films Under Solar Light Irradiation .......................................................... 545
Masaaki Kitano, Masato Takeuchi, Masaya Matsuoka, Michio Ueshima, and Masakazu Anpo

24  Construction of Solid-State Thin Film Solar Cell by Applying Visible Light-Responsive TiO$_2$ Thin Film Materials ................................................................. 561
Masaya Matsuoka, Masayuki Minakata, Afshin Ebrahimi, Masakazu Anpo, Hung-chang Chen, and Wen-ting Lin

Part VII  Photocatalytic Organic Syntheses

25  Photocatalytic Transformations of Sulfur-Based Organic Compounds ................................................................. 579
Alexander V. Vorontsov and Panagiotis G. Smirniotis

26  TiO$_2$-Based Photocatalysis for Organic Synthesis ...................... 623
Vincenzo Augugliaro, Tullio Caronna, Agatino Paola, Giuseppe Marci, Mario Pagliaro, Giovanni Palmisano, and Leonardo Palmisano

27  Photocatalytic Organic Syntheses ........................................ 647
Hisao Yoshida
Part VIII  Renewable Energy from the Photocatalytic Reduction

28  Renewable Energy from the Photocatalytic Reduction
    of CO₂ with H₂O ........................................................................... 673
    Jeffrey C.S. Wu

Part IX  Photofunctionalization

29  Photofunctionalization of TiO₂ for Optimal Bone-titanium
    Integration: A Novel Phenomenon of Super Osseointegration ....... 699
    Takahiro Ogawa

Part X  Conclusions and Emerging Applications

30  Emerging Applications of TiO₂ -Based Composites .................... 717
    Prashant V. Kamat and Masakazu Anpo

Index ..................................................................................................... 741