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Steven L. Suib
Editor

New and Future Developments in Catalysis

Catalysis for Remediation and Environmental Concerns

NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

CATALYSIS FOR REMEDIATION AND ENVIRONMENTAL CONCERNS

Edited by

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NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

Introduction

The area of environmental science continues to develop as more and more effects of pollutants and wastes are known. The area of environmental remediation using catalysts is somewhat in its infancy but driven by the desire to reclaim land and water that needs cleansing. Catalysts are a key strategy for remediation and enhancing various environments. Catalysts are also crucial in the production of new materials and chemicals. There is an ever-present need for developing new environmentally friendly methods of syntheses, devices, and processes.

The use of nano-size materials for catalytic oxidation of organic pollutants is continually being developed. Photocatalysis is a method that has been proposed for quite some time and this is being applied to several environmental pollutants of air and water. Heterogeneous catalysts activated thermally are also being studied. Another chapter in this book focuses on clean and greener methods such as the use of microwave activation to promote cleaner syntheses of catalysts and catalytic processes.

Catalytic processes used for generation of clean fuels are summarized. Abatement of NO_x and emissions control are the subject of a few chapters. Catalytic convertors are discussed as well as next-generation systems. Electrochemical methods for post-treatment of auto-exhaust and for cleaning of air are proposed. A chapter focused on air pollutant abatement is presented including worldwide levels of pollutants and expectation for future cleanup. Use of biological materials for remediation especially of halogenated hydrocarbons is discussed. Organocatalysis via homogeneous catalysis to make asymmetric products is another chapter.

The area of development and use of catalysis for environmental purposes will clearly be ongoing for quite some time. There are more and more regulations that demand cleaner environments. Such efforts will improve our health and well-being and provide new pathways for making useful chemicals, fuels, medicines, pharmaceuticals, and other materials. These efforts are also focusing on improving the quality of our environment. The future is bright for these areas of research and this book provides a variety of clever approaches currently being used and developed to improve the nature of our environments.

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CHAPTER

1

Photocatalysts for Elimination of Toxins on Surfaces and in Air Using UV and Visible Light

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1.1 INTRODUCTION

Over the last several decades there has been great concern about environmental pollution due to the fact that it is one of the primary causes for various health problems as well as for possible changes in the global climate. Generally, environmental pollution can be defined as contamination of air, water, and land due to manmade waste and can be divided into three major groups: air pollution, water pollution, and soil pollution. From these three major groups, air pollution has received the attention of many researchers due to the seriousness of the impact on climate change, acid rain, smog, and human and animal health. Air pollution can be subgrouped into two main categories: as indoor and outdoor. Both categories are equally important as they can create very unhealthy conditions to humans as well as to animals and plants [1].

These environmental problems are related to energy use, and clean renewable energy is needed, such as solar energy, wind, geothermal, etc. Out of all these renewable energy sources, solar energy has the most potential. In fact, it has been calculated that the amount of solar energy arriving at the earth's surface in a minute is sufficient to meet the energy demand of the world for a year. But, the lack of efficient solar energy harvesting and storing methods is one of the main drawbacks that we face. So, there are thousands of researchers around the globe experimenting on efficient methods to harvest and store solar energy. Solar energy can be used to heat or to produce electricity. Solar energy can also be converted into chemical energy or can be used to catalyze important reactions [2].

Photocatalysis is one of the very successful and active areas of research that have provided important ways to harvest readily available solar energy to destroy harmful organic air contaminants to overcome environment pollution. Usually, any chemical reaction requires a certain

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amount of activation energy to initiate the reaction. In normal chemical reactions the activation energy will usually be supplied by simple methods such as heating, mechanical stirring, etc. But, in photochemical reactions, light is used for this purpose. Upon exposure to certain wavelengths of light, photocatalytic material can be used to catalyze specific chemical reactions based on the oxidation and reduction potentials of the photogenerated charge carriers. Thus, in photocatalytic reactions, the catalytic material plays an intermediate role in absorbing light energy and promoting desired chemical reactions. According to the literature, various photocatalytic materials have been employed to drive water splitting to produce hydrogen and oxygen gases, mineralizing harmful organic pollutants, as well as to remove organic dye molecules from industrial effluents. Even though, there are many materials that have been reported, the number of materials that have become successful on an industrial scale is very limited [3].

There are various factors that determine the efficiency of a photocatalyst. These are efficiency of charge separation, energy range of the solar spectrum suitable for the excitation of the material, optimum intensity of the light photons, environment of active sites, etc. Usually, during the preparation of photocatalytic materials the energy levels of the conduction and valance bands of the materials are modified, or the chemical environment of the active site is changed by doping with suitable doping agents. These changes to photocatalytic systems usually enhance the light absorption, electron-hole pair generation, and the overall activity. Surface acidity is another important factor that determines the specificity, efficiency, and the mechanism of action of a photocatalytic material. For example, acidity of titania-based materials is strongly related to the amount of surface hydroxyl groups present on the surface and these groups play a major role in trapping photogenerated holes and thereby decrease the recombination of electron-hole pairs, which in turn increase the quantum efficiency of the photocatalyst [4].

Most of the successful photocatalytic materials that have been reported consist of a supporting base material. Usually compounds such as zeolite, titania, and silica are popular as successful base materials due to their high stability under high temperature and pressure conditions, low toxicity, low cost, and the ability to obtain various physico-chemical properties simply by changing particle dimensions. Usually the supporting material facilitates the catalytic activity of the catalytic site by enhancing charged carrier separation, providing reduced electron-hole recombination, and facilitating charge transfer to an adsorbed species [5].

On the other hand, most of the catalytic systems reported in the past are primarily based on at least one semiconducting base material. Semiconducting materials are required to obtain good photocatalytic activities due to the ability of semiconductors to create reactive electron-hole pairs upon irradiation of UV or visible light. But, whether comparable photocatalytic activity can be obtained without using semiconducting base materials is an important question that still remains unanswered. Thus, it is very important to directly compare other available options, such as insulator-based materials, in order to determine the photocatalytic activities of these materials.

1.2 TITANIUM DIOXIDE-BASED PHOTOCATALYSIS

Titanium dioxide photocatalysis is the most studied and well-understood photocatalytic system. Thus, studying the mechanistic details of how titania behaves is important. Titanium dioxide, also known as Titania, is a white-colored compound that is widely used as a photocatalyst, catalytic support, sensor material, and hydrogen adsorber. Titania is a semiconductor with a band gap of 3.2 eV, and has been shown to promote mineralization of organic pollutants, water splitting, and carbon dioxide reduction upon exposure to UV light. Titanium dioxide occurs in nature in three well-known mineral forms known as anatase, rutile, and brookite. Among these mineral forms, anatase typically exhibits higher photocatalytic activity than the other two forms. But, in some cases it has been reported that even higher photocatalytic activity is possible with precise mixtures of both anatase and rutile. One such example is commercially available Degussa P25 TiO_2, which consists of 80% anatase phase and 20% rutile phase. Because of a relatively wide band gap, titania absorbs light corresponding to wavelengths shorter than 388 nm, which is only 3–4% of the solar energy that reaches the earth. Thus, in principle, photocatalytic activity should be enhanced by adjusting the band gap toward visible light energies by doping, since visible light is readily available in the solar spectrum. Doping has been carried out in earlier research using various methods and materials. Common doping materials used have been inorganic compounds, noble metals, transition metal oxides, organic dye molecules, anionic compounds, etc. [5–7].

1.2.1 Non-Metal Doping

Doping with various non-metallic compounds has been carried out to obtain visible light photoactivity of titania photocatalysts usually by introducing new energy states in between the band gap. Low-band gap, nitrogen-modified titania-based visible light photocatalysts prepared by Kisch and coworkers and Panayoto and coworkers are good examples of photocatalytic materials based on titania that has been doped with non-metallic material. According to these reports, nitrogen-doped titania photocatalyst clearly shows an intense band-to-band absorption in the range of 400–500 nm visible range of the solar spectrum, which brings the modified band gap of titania to 2.46–2.20 eV and very high photocatalytic activity toward formic acid mineralization under visible light (Figure 1.1) [8,9].

Tang and coworkers also reported on highly crystalline and ordered mesoporous TiO_2 thin films doped with carbon, synthesized via a highly cost-effective route, that exhibit high

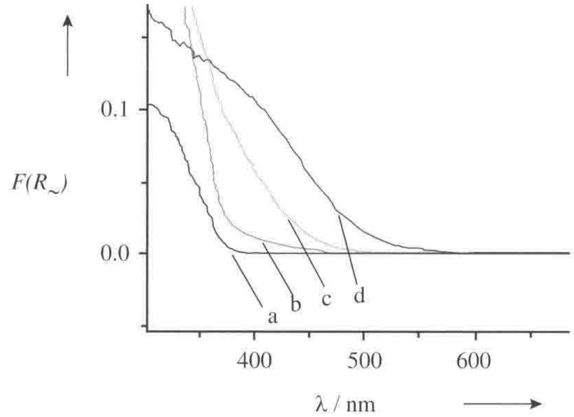

FIGURE 1.1 Diffuse reflectance spectra of (a) TiO_2, (b) TiO_2–N, (c) TiO_2–N1 calcined 1 h, and (d) TiO_2–N_2 calcined 0.5 h [8].

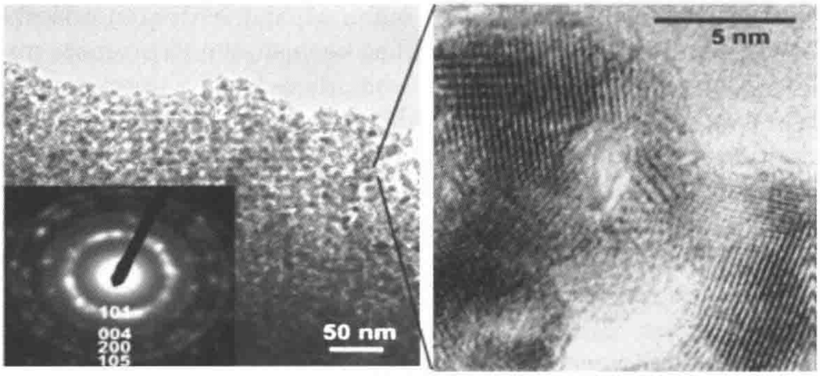

FIGURE 1.2 TEM images of a TiO_2 thin film crystallized at 550 °C with pure post-induced carbon as the confining material. The zoom-in image is also shown on the right. The inset is a selected area electron diffraction pattern (SAED) indexed as the anatase phase [10].

photocatalytic activity. In this material carbon inclusion plays a major role to stabilize the framework of titania during thermal crystallization process. Moreover, according to their findings high crystallinity and ordered mesoscopic structures always help to enhance the efficiency of photocatalysis [10] (see Figure 1.2).

Further, there are reports about titania-based photocatalytic materials co-doped with several non-metallic compounds. Xiang and coworkers as well as Hamal and coworkers have separately reported successful preparation methods for visible light active titania photocatalysts using more than one non-metal [11,12]. According to the literature, doping with nitrogen and sulfur co-dopants can induce the formation of new energy levels in the band gap. These new energy levels result in visible light response of co-doped photocatalysts due to the requirement of lower energy of photons to generate new electron-hole pairs. Under lower energy visible light irradiation, electrons can easily transfer from the valance band to impurity states, and the electrons in the impurity states can move to the conduction band after secondary excitation [12]. The density of states diagram represented in Figure 1.3 clearly indicates the insertion of intermediate energy levels due to the addition of S and N [12].

1.2.2 Metal Doping

Visible light photodegradation activity of titania can also be obtained by introducing various metals and metal oxides. Transition metals and respective metal oxides have been actively used in this regard due to the ability to absorb in the visible range of the spectrum, as orbital energy transfer usually lies in the matching wavelength range. There are a large number of reports about effects of metal-ion doping on titania photocatalysis. Some metal ions like Co^{3+} and Al^{3+} decrease the photocatalytic activity while metal ions such as Fe^{3+}, Ru^{3+}, V^{4+} enhance the photocatalytic activity. According to Choi and coworkers the relative photocatalytic efficiency of a metal-ion dopant depends on whether the metal ion serves as a mediator of interfacial charge transfer or a recombination center [13]. Furthermore, they have carried out an interesting study of titania-based photocatalysis using various metal-ion dopants to study the effect of each dopant on visible light photocatalytic activity of titania prepared by

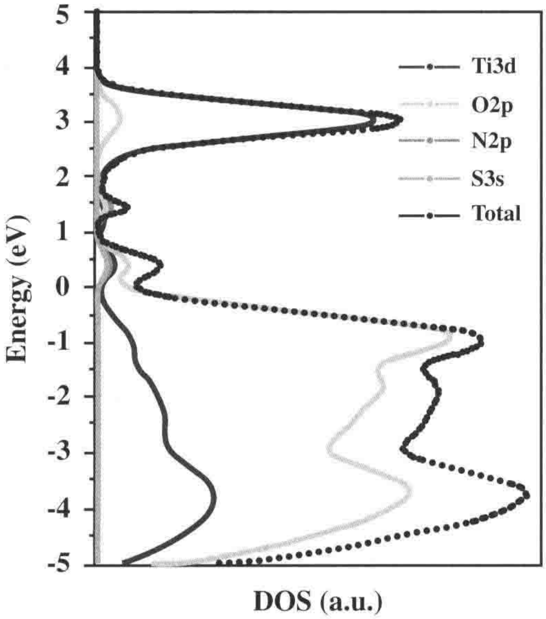

FIGURE 1.3 Total density of states for N,S co-doped TiO_2 at 2.08 at.% doping levels [12].

the well-known sol-gel method [13]. According to the findings of Choi and coworkers, the ionic radii of the dopant metal ion play an important role in the final structure of the photocatalytic material and have a direct effect on the photoactivity. The final structure of a doped photocatalyst is highly affected by the nature of the doped metal ion and its size. Usually, metal ions such as Pt^{4+}(0.765 Å), Cr^{3+}(0.755 Å), and V^{3+}(0.78 Å) ions, which have similar ionic radii to Ti^{4+}(0.745 Å) ions in titania, are most likely substituted in the titania framework with less amounts of distortions, thus forming favorable structures. In contrast, metal-ion dopants such as Co^{2+}(0.89 Å), Cu^{2+}(0.87 Å), and Pt^{2+}(0.94 Å) ions usually end up located in interstitial positions of the titania lattice, rather than directly in Ti^{4+} sites, because of the relatively large size difference between dopant ions and Ti^{4+}. Also, much larger dopant ions such as Ag^+, Rb^+, Y^{3+}, and La^{3+} ions do not get incorporated in the titania framework due to the larger size variation between the metal ion and Ti^{4+}. Thus, they are more likely to be found as dispersed metal oxides within the crystal matrix or dispersed on the surface of TiO_2 [13].

Usually, visible light activity in metal-ion doped titania aerogels can occur due to two main reasons: (1) the excitation of electrons from the dopant ions to the conduction band of titania (i.e., a metal to conduction band charge transfer) or (2) defects associated with oxygen vacancies that give rise to colored centers, or a combination of both. However, the changes that occur to titania due to dopant metals can be clearly identified using diffuse reflectance UV-Vis studies, as reported by Choi and coworkers (Figure 1.4). According to their observations there is no significant difference between the absorption spectra of pure titania and Ag, Rb, Y, and La ion-doped titania samples, since these larger ions did not incorporate into the titania framework (spectra are identical to undoped TiO_2). But in Figure 1.4a–c it is very clear that the metal ions of similar size as Ti^{4+} have successfully been incorporated into the matrix of titania creating additional bands which induce absorption in the visible range of photons [13,14].

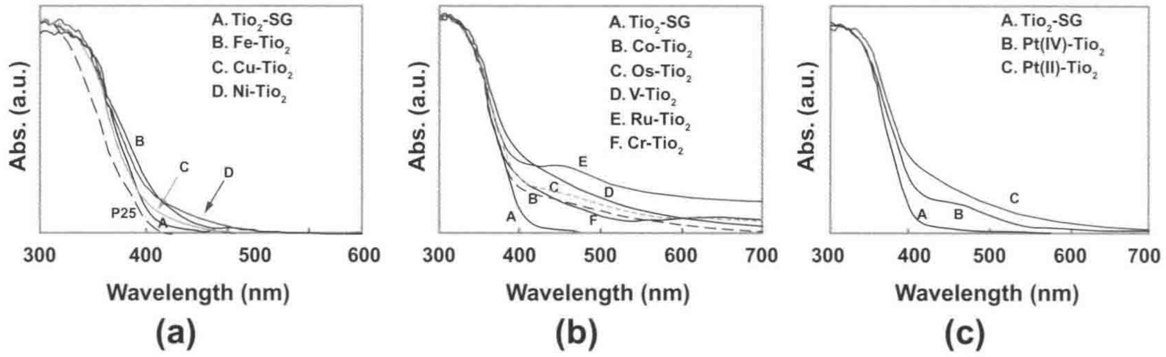

FIGURE 1.4 UV-Vis diffuse reflectance spectra for various metal-TiO_2 samples. Absorption spectra for Ag^+, Rb^+, Y^+, and La^+ TiO_2 samples, which are not shown here, are identical with that of undoped TiO_2 [13].

Rates of the mineralization of various organic pollutants using photocatalysis have been obtained by many researchers. Titania-based photocatalysts have been employed mainly in oxidation catalysis. There are reports about polymerization mechanisms and reduction mechanisms as well. According to the collective results of photocatalytic activities of titania reported in the literature, metal-ion doping seems to be not important under UV light, as the increases in the activity compared to pure titania-based samples are very small. Under UV light irradiation, the majority of the reactive species are created by semiconducting titania itself. But when it comes to visible light active titania photocatalysts, doping agents play an important role by introducing additional energy levels within the band gap of titania, introducing trap states, and by stabilizing the titania framework [13,14].

The next topic to be discussed is the chemistry that photocatalysts induce. The study of hydroxyl radical generation upon exposure to UV light is widely used to confirm the mechanism of photocatalytic activity of titania-based photocatalysts [15–17]. According to the reported results of hydroxyl radical detection experiments, titania-based samples clearly indicate the formation of hydroxyl radicals upon exposure to UV light and visible light (Figure 1.5).

Since titania is a semiconducting pigment, its valence electrons can be promoted into the conduction band, resulting in the formation of an electron-hole pair upon irradiation with suitable light. But, the created electron-hole pair needs to be spatially separated in order to allow the formed electron-hole pair to undergo chemical reactions. In titania, charge carrier recombination is usually avoided by immobilizing the created excited electron or hole or both in the trap states available in between the conduction and valance bands [7]. Formed excited electrons usually have a higher effective mass compared to the holes, and moderate reduction potential. So, electrons tend to remain in their free state or in some cases get trapped at the surface. On the other hand, holes usually have high oxidation potential and get trapped at the semiconductor surface. Usually a light excited hole can follow two paths. The holes either oxidize the hydroxyl groups available on the surface of titania to produce hydroxyl radicals, or oxidize lattice oxygen atoms from −2 to 0 valence state to create oxygen vacancies in titania. Therefore, in supported photocatalytic materials titania plays two major roles by itself providing a support to the system as well as providing active catalytic sites. Thus, the entire

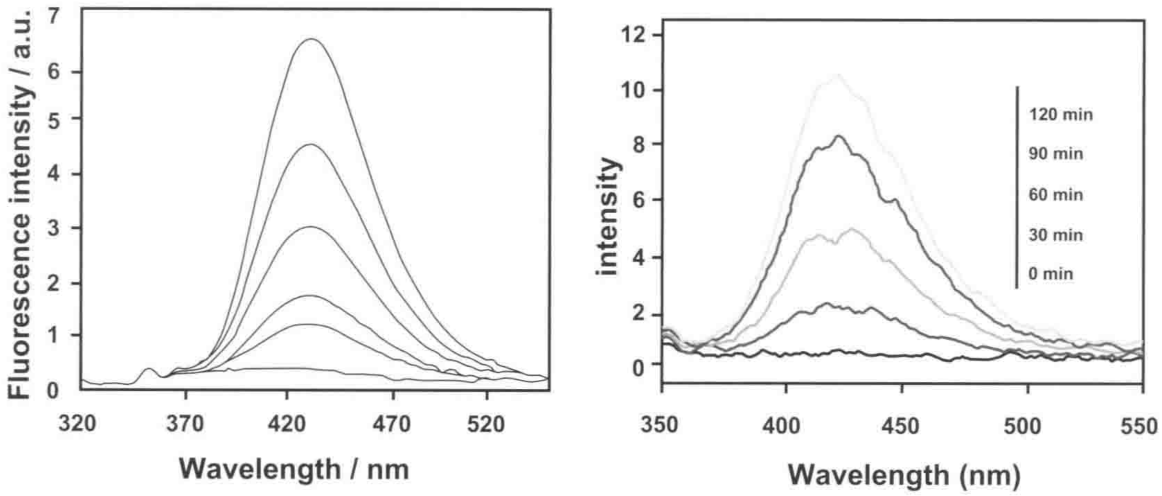

FIGURE 1.5 Fluorescence spectra obtained for the supernatant liquid of the irradiated TiO_2 suspension containing terephthalic acid at various irradiation periods PL spectral changes with irradiation time under UV and visible light [15,17].

material is involved in photocatalysis, making the photocatalysis process non-localized [18].

Therefore, according to the general mechanism of titania-based photocatalysis, upon exposure to UV light positively charged holes and negatively charged electrons will be created in valence and conduction bands of titania respectively as described by Eq. (1.1):

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^- \text{ and } h^+), \tag{1.1}$$

$$h^+_{vb} \rightarrow h^+_{trap}, \tag{1.2}$$

$$O_2 + e^- \rightarrow O_2^{\cdot -}. \tag{1.3}$$

In the second step positively charged holes will be trapped by surface hydroxyl groups of titania generating reactive hydroxyl radicals (Eq. (1.2)). In the meantime negatively charged electrons in the valence band can interact with oxygen gas to generate reactive oxygen species (Eq. (1.3)). The oxidation ability of $^{\cdot}OH$ radicals is very high so that they can easily react with various organic pollutants according to various reaction schemes [15,19]:

$$O_2^{\cdot -} + O_2^{\cdot -} + 2H^+ \rightarrow H_2O_2 + O_2, \tag{1.4}$$

$$O_2^{\cdot -} + h^+_{vb} \rightarrow O_2, \tag{1.5}$$

$$O_2^{\cdot -} + h^+_{trap} \rightarrow O_2, \tag{1.6}$$