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Preface

As early as 1969, a groundbreaking study informed to launch rigorous research activity on the reactivity of photoactivated semiconductor catalysts coined photocatalysis. Staring the decades of development, research activities have come a long way in accomplishments. Currently, articles in different aspects of photocatalysis abound most scientific journals and libraries. Such advances brought forth will inform the decision to as well publish more books. The present book underscores many of the essential grounds of photocatalysis and provides updates on the scientific cornerstones, research advances, current opinions and interpretations. Basically, the book is devoted only to photocatalysis by semiconductor materials. Therefore, in major discussions other photocatalysts such as phthalocyanines will not at all be considered. Our emphasis is on treating topics essential for understanding the current drive in photocatalytic research.

We began our discussion of photocatalysis in Chapter 1 by introduction of the concepts that form the backbone of photocatalysis. The chapter covers the principles of solid state chemistry and physics underlying photocatalysis including the concept of semiconductivity, band gap calculations, defects and reactive oxidising species. Photocatalysis has an organic link with chemical kinetics and leads unifying investigations where all the branches of science cross-pollinate. Chapter 2 of the book therefore describes kinetic concepts as they apply to photocatalysis. In this chapter, the dependence of rate on reaction conditions and parameters has been detailed. Chapter 3 deals with mechanism of photocatalysis. Aspects of physical chemistry such as adsorption models, photocatalytic rates and kinetic disguises have been discussed. Chapter 4 focuses on the structure, property and activity of prototypical semiconductor photocatalysts. One poser that is invariably raised is how to extend the spectral absorption of TiO_2 to visible region to enable the effective use of visible solar spectrum. This chapter discusses the strategies to drive substantially improved photoactivity from semiconductor materials. The factors affecting performance of photocatalyst have been highlighted.

The goal of environmental photocatalytic oxidation is to eradicate air and waterborne pollutants. Chapter 5 presents a recent survey of persistent pollutants, which is aimed at helping to provide perspective or update to researchers. As most workers have used various photocatalysts, model pollutants, physical state of reactant, reactor configurations and conditions, this chapter brings to notice the useful findings. Besides environmental purification, photocatalysis finds viable applications in chemical analysis and alternative energy. The chapter also devotes discussions on recent topics in the applications of photocatalysis such as remote photocatalytic oxidation, intelligent ink indicator and dual function photocatalysis. Chapter 6 focuses on the advances that relate to organic chemistry especially as regards synthesis, product selectivity and characteristic reactions. Finally, this text utilises current terminologies and acceptable illustrations in the aspects of physical chemistry of heterogeneous photocatalysis in order to guard against misconceptions.

Readership: This book would appeal to students, and researchers in the industry and academia, who may be interested in applied physical chemistry and related fields in the mainstream chemistry tandem. I hope the book will be extended to the bookshelves of myriad libraries for extensive dissemination of knowledge.

Acknowledgements

If charity really begins at home, I will start my acknowledgements from home. I am grateful to my father Alhaji Ibrahim Abdulkadir Gaya, and my late mother Hajiya Fatima Ibrahim, for their love and care. I owe debt to my wife who endured the unpleasant period of writing this book. I express my gratitude to all brothers, sisters and friends who continuously wish me the best of academic carrier.

Many people have assisted in the success of this project in one way or another. I wish to start my acknowledgements by expressing gratitude to various workers who provided permission to reuse their illustrations in this book. To mention, I gratefully acknowledge the assistance of Professor Michael Grätzel, the father of the famous Grätzel cell and the Director of Photonics and Interfaces Laboratory, Ecole Polytechnique Federale de Lausanne, Switzerland. Accordingly, I express gratitude to Professor Naoto Tamai, Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Japan. I owe heaps of thanks to Professor Hadis Morkoç of the Department of Electrical Engineering and Physics Department, Virginia Commonwealth University, Richmond, USA. Similarly, I thankfully acknowledge the support of Prof. Russell Howe, the Head of the Department of Chemistry, University of Aberdeen, UK and Professor Shizang Qiao of the ARC Centre of Excellence for Functional Nanomaterials, University of Queensland, Australia and Prof. Dr. H.G. Yang of the Key Laboratory for Ultrafine Materials, School of Materials Science and Engineering, East China University of Science and Technology, China. I also wish to acknowledge the American Chemical Society, Elsevier, Royal Society of Chemistry, and Taylor and Francis Group for permission to reuse copyright materials.

I am quite indebted to all my colleagues in Bayero University Kano, and in other places I dwelled for different academic pursuits for all fruitful discussions we had before and while writing this book. Special thanks to Dr M.A. Kurawa, the present Head of Pure and Industrial Chemistry Department, Bayero University Kano, as well as other members of the department. I thank Dr Abdul Halim Abdullah and Professor Zulkarnain Zainal, the former Heads of Department of Chemistry, and Professor Taufiq Yun Hin and Professor Mohd Zobir Hussein, the former and the current Heads of the Putra Centre of Excellence for Catalysis Science and Technology (PutraCat), for their useful advice during my days as student at Universiti Putra Malaysia. I wish to express gratitude to Professor Detlef Bahnemann of Institut fur Technische Chemie, Gottfried Wilhelm Leibniz, University of Hannover, Germany, for sharing with me sometimes earlier a few of his publications on doped titania materials and on the preparation of brookite. Finally, I gratefully acknowledge the time and energy allocated by those who participated in the blind review of this book, and the staff of Springer who interfaced with me.

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Contents

Acronyms and Symbols

AC	activated complex
A_s	specific surface area of reactor
BET	Brunauer-Emmett-Teller
CB	conduction band
CVD	chemical vapour deposition
D	diffusion coefficient of charge carrier (or effective diffusivity)
d	size of the semiconductor particle's cross-section
DRS	diffuse reflectance spectroscopy
E	applied electric field
E^*	apparent activation energy
E_F	Fermi-level energy
E_g	band gap energy
E_i	ionisation energy
E^o	standard oxidation potential
EPR	electron paramagnetic resonance
FID	flame ionisation detector
FWHM	full width at half maximum
g	electron g-factor
GC/FID	gas chromatography/flame ionisation detector
GC-MS	gas chromatography-mass spectroscopy
H	thickness of semiconductor film
HPLC	high performance liquid chromatography
IR	infrared
J	current density
k	rate constant
K	Boltzmann constant
k'	pseudo order rate constant
$\mathrm{K_{ads}}$	adsorption constant
k_m	fluid to surface mass transfer
L	crystallite particle size
LDPE	low density polyethylene
m	evaporation rate

NMR	nuclear magnetic resonance
P.E.	potential energy
$\mathrm{p}K\mathrm{a}_1$	negative log of first acid dissociation constant
$\mathrm{p}K\mathrm{a}_2$	negative log of second acid dissociation constant
PVD	physical vapour deposition
R	molar gas constant
r	radius
r	rate of reaction
R	size of agglomerate
RF	radiofrequency
ROS	reactive oxidising species
SAED	selected area electron diffraction
SC	semiconductor
TEM	transmission electron microscopy
TOC	total organic carbon
TON	turn over number
UV	ultraviolet
VB	valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
α	absorption coefficient
ε	permittivity of space
η	optimal catalyst domain
θ	diffraction angle
θ	surface coverage
μ	viscosity
μ_B	Bohr's magneton
ν	frequency (of light or light absorption)
ξ_{r}	relative photonic efficiency
ρ_{sc}	density of semiconductor photocatalyst
σ	conductivity or surface charge density
τ	fractional lifetime or half-life
ϕ	probability of light absorption to produce charge carriers
Φ	quantum yield (or thiele modulus)
ϕ_{eff}	photocurrent efficiency
φ_L	light harvesting efficiency
ω	angular velocity

Chapter 1
Principles of Heterogeneous Photocatalysis

Abstract At the turn of 1970s, the photo-response of solid materials became a constant subject of intensive research for possible application in modern technologies. Heterogeneous photocatalysis has evolved in a unique way giving rise to various applications for alternative energy, organic synthesis and environmental treatment. Semiconducting compounds have thrived as the most suitable materials for these applications. Towards achieving the maximum potential benefits of semiconductor photocatalysis and to make remarkable impact, the fundamental concept as well as application has been extensively and rigorouslyexplored. We therefore detail herein the basic formalism of semiconductor photocatalysis from band models through the generation of oxidants to the light harvesting processes. The key imperfections in semiconductor oxides and their consequences on the extrinsic semiconductivity are outlined. The advances being made regarding the role of oxidising species in photocatalytic degradation are rationally discussed. Finally, the reader is referred to some 'must read' articles in heterogeneous photocatalysis by semiconductor solids.

1.1 Background Sketch

The interaction of light with molecules and the resulting processes are currently of major interest in the development of various chemical technologies. Various types of semiconductor catalysts are known to be photosensitive, allowing activation by light photons. Phoactivated molecule may initiate or influence the rate of chemical reaction by energy or charge carrier transfer. Such molecules are known as photocatalysts and they form the backbone of heterogeneous photocatalysis. Heterogeneous photocatalysis has gained acceptance as a viable alternative to traditional biological, chemical and physical decontamination technologies owing to its striking attributes for exploitation in environmental context, which include non-selectivity, non-toxicity, total removal of pollutant and by-products, and cost-effectiveness (Tai and Jiang 2005; Doong et al. 2000; INERIS 2005; Muruganandham et al. 2006; Saien and Soleymani 2007).

The world has constantly been witnessing advances in the manufacture and use of synthetic chemicals. Regrettably, a high number of these chemical substances are

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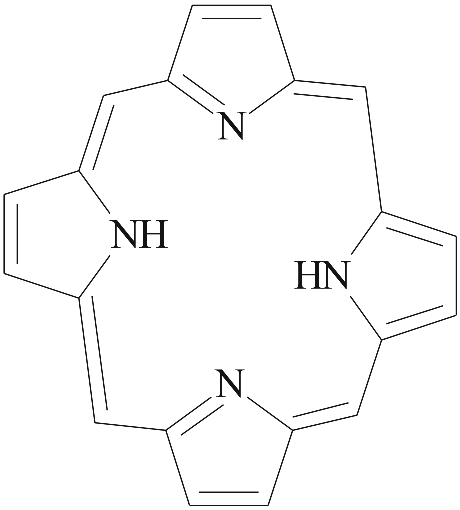
known to have severity of toxicity to both plants and animals (Pelizetti et al. 1990; Abramović et al. 2004). Certainly, the environmental implication of such hazardous substances cannot be tolerated. Against this background, environmental agencies have periodically come up with legislations to guide the use of synthetic chemicals and release of waste (David 1995; Saxena and Jotshi 1996; Carp et al. 2004). In spite of these stringent regulatory measures however, pollution has become widespread owing to varied nature of wastes, contributory negligence to control the use of waste chemical products or poor efficiency of treatment technologies.

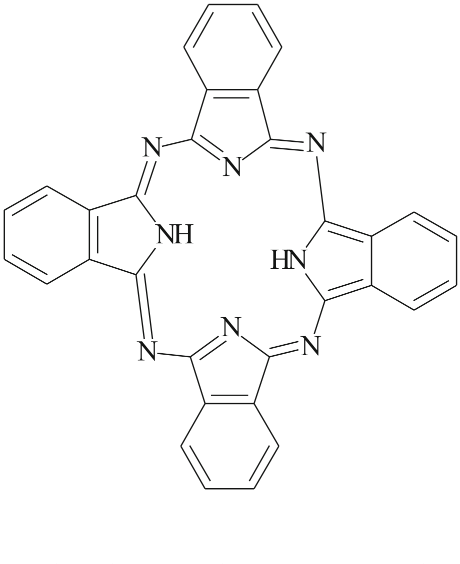
Several environmental pollutants have become prominent, among which dyes and halophenols stand in the forefront owing to their widespread uses. About 1–20 % of the world production of dyes is loss during the dying process (Kabra et al. 2004; Augugliaro et al. 2006). The chemical nature and stability of these synthetic dyes spells serious threat to the environment. Similarly, since 1930s halophenols have been used as chemical intermediaries, wood preservatives, miticides, pesticides, herbicides and as defoliants (Herrmann 1999; Lewis 2002). About 85 % of these organic wastes may be found in surface water (Pohanish and Green 1996). Well aware of the implications of hazardous substances, scientists have continually developed methods which could serve to remove these important pollutants from the environment. Several conventional methods therefore exist which include adsorption and thermal oxidation. In retrospect, many of these traditional treatment methods have been identified with various disadvantages such as non-destructiveness (US EPA 2006), poor rate of removal at higher concentration (EPA 1998), high cost or ineffectiveness at low pollutant level (US EPA/OSHA 2000).

Photocatalysis is a chemical jargon conventionally defined as the acceleration of the rate of a chemical reaction, induced by the absorption of light by a catalyst or coexisting molecule. This may be the most widely accepted definition of photocatalysis as it encompasses all aspects of the field including photosensitisation (Serpone and Salinaro 1999; Braslavsky 2007). Photosensitisation is the light-induced alteration of a molecular entity as a result of photoabsorption by another molecule (the photosensitizer). Although the initial molecule does not absorb light, this phenomenon can still be classed under photocatalysis provided that it exhibits catalytic nature. That is to say the photosensitizer must bring about a positive change in quantum efficiency (Ohtani 2008). Generally, a photocatalyst is a material that can induce reaction upon efficient light absorption. The number of available photocatalysts is high, and these photocatalysts may be categorised into semiconductor-based, composites, complex oxides, polyoxometallates and complex organic or organometallic compounds such as porphyrin, pthalocyanine, metalloporphyrins and metallophthalocyonines.

Phthalocyanine is synthetic macrocyclic derivative of porphyrin having an extended π-electron system **(1)**. When phthalocyanine **(2)** is complexed by a metal (with the metal in the centre of the macrocycle) the resulting derivative is called metallophthalocyanine. Several transition metal phthalocyanine complexes are known and they tend to be more resistant than porphyrin itself. Phthalocyanine and metallophthalocyanines possess photocatalytic activity for a wide variety of reactions. These substances qualify further as heterogeneous photocatalysts for organic pollutant removal owing to their poor solubility in both organic solvents and water. From synthesis point of view, the preparation of metallopthalocyanines is quite simple. For example, zinc phthalocyanine can be facilely prepared by condensation of phthalic anhydride in presence of urea.

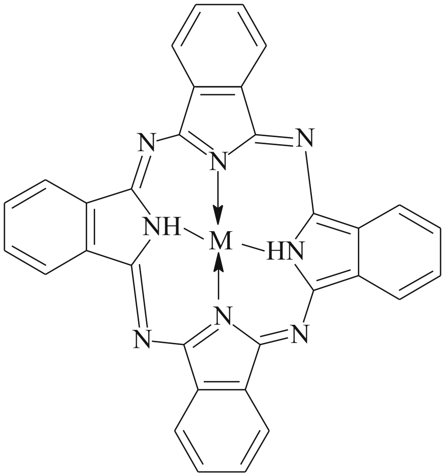


(1)



(2)

The mechanism by which giant organic or organometallic molecules serve as photocatalysts is simply photosensitisation. Metallophthalocyanine (MPc) (3) can be excited to singlet state (^{1}MPc*) by irradiation, which through intersystem crossing moves to the triplet excited state (^{3}MPc*). The triplet state then interacts with ground (triplet) state molecular oxygen ($^3O_2$) to generate excited singlet oxygen ($^1O_2$) for the oxidation of organic molecules as shown in the reactions (1.1) to (1.4).



(3)

$$MPc \xrightarrow{h\nu} {}^1MPc^* \tag{1.1}$$

$${}^1MPc^* \xrightarrow{\text{intersystem crossing}} {}^3MPc^* \tag{1.2}$$

$${}^3MPc^* + {}^3O_2 \rightarrow MPc + {}^1O_2 \tag{1.3}$$

$$\text{Substrate} + {}^1O_2 \rightarrow \text{oxidation products} \tag{1.4}$$

The use of phthalocyanines as photocatalysts for environmental decontamination suffers some drawbacks. Even though several metallophthalocyanines can be listed (with central metal as Zn, Al, Si, Co, Ni, Cu or Ti) only the aluminium, silicon and zinc -based counterparts were sufficiently photocatalytically active (Kluson et al. 2007). Several workers have therefore attempted the enhancement of photoactivity of the metallophthalocyanines by the use of support materials in the case such as polydivinyl benzene (Wu et al. 2007), TiO_2 and Al_2O_3 (Iliev 2002). Besides, phthalocyanines and metallophthalocyanineslo present real perspectives as photocatalysts because their relative stability depends on their molecular structure and whether supported or not (Mele 2003).

Polyoxometallates have been investigated as homogeneous photocatalysts for photocatalytic degradation of organic substances. Polyoxometallates (POMs) are molybdates and tungstates of the Keggin structure (composing of Keggin anion $[XMo_{14}O_{24}]^{n-}$ where $X = P$, Si, Fe, H_2), Dawson type structure (composing of $[P_2W_{18}O_6]^{6}$) or similar structure. So, we can have a polyoxometallate from Keggin anions such as $[SiMo_{14}O_{24}]^{4-}$, $[PMo_{14}O_{24}]^{3-}$ while cations may be H^+, K^+, Na^+ or $NH_4{}^+$. The molecular excited states of the molecules in the reactivity system (the lowest unoccupied molecular orbital, LUMO and the highest occupied molecular orbitals, HOMO) initiate an electron tranfer process via which efficient photodegradation may take place. For instance, the photodegradation of 2-mercaptobenzothiazole has been studied using a polyoxotungstate ($Na_4W_{10}O_{32}$) (Allaoui et al. 2010). The POM increased the rate of 2-mercaptobenzothiazole relative to photolysis by 6 times. The disadvantage of the use of POMs as photocatalysts stems from the fact that they are highly soluble in polar solvents.

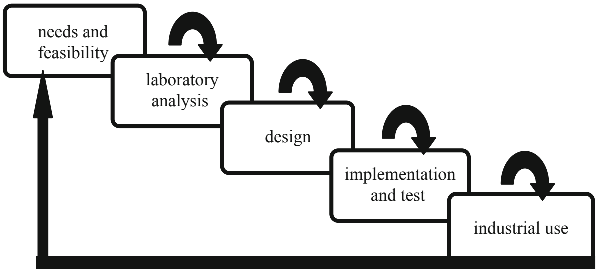
Relatively, inorganic semiconductors have been recognised as the most successful photocatalysts for various forms of applications. These substances occur in the form of oxides, sulphides, composites and complex oxides. Some notable examples of these semiconductor solids used in environmental heterogeneous photocatalysis include TiO_2, ZnO, CdS, WO_3, SnO_2, ZnS, CdTe, CdTe, α-Fe_2O_3, $AgNbO_3$ and $SrTiO_3$. These compounds demonstrated rich photochemical properties for harvest. For instance, CdS can absorb most part of visible light owing to its short band gap (2.42 eV) which makes it a potential photocatalyst for solar cells and photocatalysis. However, this material is not very stable under photocatalytic condition. Similarly, ZnO exhibits several important characteristics such as piezoelectric properties and extended spectral absorption. This photocatalyst has sometimes surpassed TiO_2 in terms of photocatalytic efficiency but a problem associated with it is propensity for photodissolution.

By far, TiO_2 and TiO_2-based materials have been identified as the most economically attractive and authoritative photocatalysts owing to properties like non-toxicity, cost-effectiveness, ready availability, chemostability, reusability, outstanding electronic and optical characteristics. Consequently, there are various purposes for which this inorganic semiconductor can be used. Worth mentioning here are environmental cleaning, solar-energy conversion, photodisinfection and photokilling of cancer cells. In the environmental cleaning context, TiO_2 is used in self-cleaning glasses and in the mineralisation of aqueous or air borne pollutants. The disinfection of water and air from microorganisms can also be achieved by TiO_2 photocatalysis. A good example of the use of titania in energy applications is the dye-sensitised photovoltaic cells. This cell consists of TiO_2 duedue to its superior applicability which includes resistance to photocorrosion (Desilvestro et al. 1985; Argazzi and Bignozzi 1995; Tachibana et al. 1996). At the moment, photocatalysis has become a point of focus where innumerable disciplines converge.

Semiconductor-mediated heterogeneous photocatalysis has appeared in various forms and has therefore attracted a high number of reports dealing with fundamental studies, integration and application (Dillert et al. 1999). In fact, a high number of patents and applications on photocatalytic technology have appeared proving its unrivalled power as an environmental treatment tool (Blake 1999). Decidedly, these projects need to be guided by what we furnish herein as the waterfall model of photocatalyticdevelopment (Fig. 1.1). Arguably, every successful photocatalytic investigation ought to go through the cyclic model.

In the first stage of the waterfall model new ideas and proposals are considered. This stage can therefore be referred to asthe feasibility stage. The next stage of the lifecycle involves laboratory analysis in order to arrive at optimised parameter conditions for successful laboratory operation. Subsequently, a design of a pilot reactor may be made and performance tests carried out. Finally, a large-scale facility

Fig. 1.1 Waterfall model for the development of photocatalytic application



can be generated. Feedbacks arising from these large-scale applications are tackled by re-cycling through the waterfall cycle.

1.2 Evolution of Semiconductor Photocatalysis

From historic point of view, photocatalysis has been an old phenomenon and its existence is apparent from common observations. Ideas on photocatalysis can be visualised from the fading of painted walls upon long-term exposure to sunlight. Fundamentally, this illustrious phenomenon takes place as a result of the photo-oxidative reactions the paint undergoes in present of the TiO_2 used as additive. Even though studies on the photoactivity of semiconductor oxides for the oxidation of substances can roughly be traced to early twentieth century, the question of where it first originated may continue to be unanswerable (Hashimoto et al. 2005). In 1921, Renz (1921) found for the first time that titanium oxide, as well as some other oxides investigated, formed dark reduction products when irradiated in the presence of a suitable organic acceptor. The utilisation of TiO_2 for the photo-decolourisation of dye was studied way back 1938 by Goodeeve and Kitchener (1938), and the oxidation of organic solvents in 1950s, by Kato and Mashio (1956). Later on Morrison and Freund (1967) studied the photocatalysed oxidation of aqueous phase formic acid in presence of ZnO which yields CO_2 and H_2O_2. With the report of CO_2 and H_2O_2, the study perhaps places ZnO the first semiconductor to be used in photocatalytic mineralisation.

It was not until 1969 when Fujishima and Honda (1972) made a groundbreaking discovery of the photoelectrolysis of water molecule using an *n*-type rutile TiO_2 anode against platinum cathode that photocatalysis came into much limelight and prompted the beginning of fervent research in the field of photon energy conversion as an alternative energy source, through 1970s to early 1980s. Subsequently, deriving useful reactions by this great phenomenon became the business of the day. Today, several applications of photocatalysis can be clearly distinguished even domestically.

1.3 Photophysics and Photochemistry

At molecular level, the interaction of the semiconductor with light is considered more or less in unified way by all workers. The core concepts of heterogeneous photocatalysis are treated in the framework of photophysics and photochemistry. However, the resulting processes and applications can be viewed from various standpoints. Many semiconductor photocatalysts would naturally be thought of to be visible-light responsive owing to their possession of colour. For instance, WO_3 and CdS have rich yellow colour are good visible light photocatalysts. The first explanation that will come to mind for their photocatalytic activity is therefore the excitation of electrons. Basically, when light is absorbed by the semiconductor photocatalyst electronic excitations take place, which can be exploited in chemical or electrical work. The nature of application of these chemical excitations may vary depending on discipline. As a result, potpourri of processes and applications has been established using various photoactive semiconductor materials.

Materials have often been classified on basis of their ability to conduct electricity mainly into three classes: conductor, insulator and semiconductor. In a conductor electrons are free to move from one site to another whereas in an insulator there is no movement of electrons at all. Semiconductors are characterised by intermediate electronic behaviour. Semiconductors have more readily understood electronic structure than conductors, usually explained by the 'band model' (Hagen 2006).

1.3.1 Band Gap Model

The atoms or molecules of a solid are grouped together in certain order as well as with their energy levels. The energy levels are grouped in form of bands. The band gap theory proposed two bands for a crystalline solid: the conduction band CB (being the lowest unoccupied molecular orbitals, LUMO; consisting antibonding orbitals) and the valence band VB (being the highest occupied molecular orbitals, HOMO; made up of bonding orbitals) which are separated by forbidden zone called the band gap. In insulators the conduction band and the valence band are separated by a large band gap. In metallic conductors however, there is apparently absence of gap between the CB and the VB owing to overlap of molecular orbitals. Semiconductors have relatively intermediate band gap and can be distinguished from insulator by band gap size. A standard of 3 eV has usually been regarded as the highest limit for the classification of semiconductors with less consistency as many semiconductors such as ZnO and TiO_2 possess larger band gaps than the standard. Perhaps it will be more appropriate to stick to the definition of semiconductor based on conductivity.

In terms of conductivity, semiconductor can be defined as a solid whose electrical conductivity (or resistivity) is intermediate between that of a conductor and an insulator (Carmen 2009). Conveniently therefore, the form of Ohm's law shown in

Eq. (1.5) can be used to distinguish between conductor, semiconductor and insulator (Richard 1995).

$$J = \sigma \xi \tag{1.5}$$

where J is the current density (A cm^{-1}), σ is the conductivity (mho cm^{-1}) and ξ is the electric field applied. Conductors and semiconductors exhibit conductivities within ranges of 10^6–10^4 and 10^{-9}–10^3 respectively, while insulators dart in the ranges of $10^6 - 10^4$ and $10^3 - 10^{-9}$ mho cm^{-1} respectively, while insulators dart in the range of $10^{-9} - 10^{20}$ mho cm−1. This classification places the conductivity of semiconductor between that of conductor and insulator with specified limits. It may be important to mention that although semiconductors do not conduct electricity at low temperature they do so at higher temperatures (Hagen 2006; Willie 2010).

1.3.2 Semiconductivity and Energetics

Semiconductivity is exhibited by ionic compounds which do not contain stoichiometric amount of metal and non-metal such as ZnO and SnO_2, or by insulators that are slightly contaminated (Castellan 1983). Three types of semiconductors may be distinguished (Hagen 2006): *i*- (or intrinsic), *n*- and *p*- (or extrinsic) semiconductors. An *i*-semiconductor is a perfect crystal semiconductor containing no impurity while *n*- and *p*- semiconductors contain impurity in their crystal lattice. Impurities in this context may also be referred to as dopants. Intrinsic semiconductors have no impurity type of imperfection but may have defects which do not affect the overall composition of the semiconductor. Defects of such type are also known as intrinsic defects. In intrinsic semiconductor, conduction occurs by thermal excitation of electrons from valence band to conduction band.

The impurities responsible for extrinsic semiconductivity can either be electron donors or electron acceptors. The introduction of an electron donor into the forbidden band of a semiconductor makes it easier for an electron to be added to the conduction band (CB) without corresponding generation of hole (h^+_{VB}) in the valence band (VB). Consequently, there is stronger presence of electrons compared to the positive holes and the resulting semiconductor is termed *n*-type semiconductor. Conversely, if an electron acceptor is incorporated into the crystal lattice of a semiconductor it becomes less easy for an electron to be added to the CB. In this case, the majority carriers are the positive holes while the minority carriers are the electrons. The resulting material is called *p*-semiconductor. In either case, the ionisation energy (E_{ion}) to eject electron from the valence band is low and can even be supplied thermally.

In the forbidden zone there exists an energy level known as Fermi, at which the probability of electron occupancy $f(E)$ is 0.5. The Fermi level lies above the donor (dopant) level of *n*-semiconductor, or below the acceptor (dopant) level for a *p*-type semiconductor. Therefore, Fermi level is closer to conduction band in *n*-type semiconductorsand closer to the valence band for *p*-semiconductor. A comparative

Fig. 1.2 Schematic diagrams showing the electron energy levels in extrinsic semiconductors: (**a**) *n*-semiconductor (**b**) *p*-semiconductor. E_{CB}, E_{VB}, E_g and E_F represent energy edges of conduction band, valence band, band gap and Fermi level

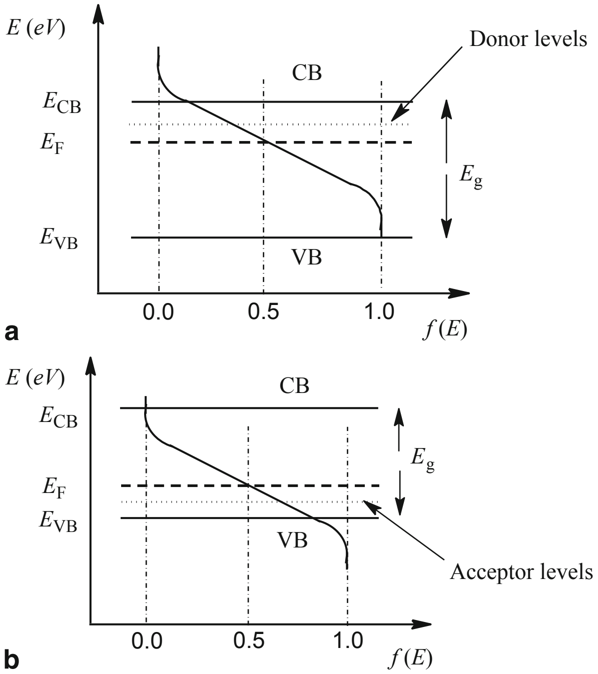


illustration of energy edges of *n*- and *p*- semiconductors is shown in Fig. 1.2. Unlike insulators, it is easy to fine tune the properties of these semiconductors to suit industrially important applications such as piezoelectricity, chemical sensors, varistors, solar cells, light emitters and as catalysts (Ozawa et al. 2005).

Semiconductor photocatalysts are a priori prepared in doped or extrinsic semiconductor form. The commonest examples of semiconductor photocatalysts such as TiO_2 and ZnO are *n*-type semiconductors. Generally, the electronic mechanism for the formation of the *n*-type or *p*-type is chemically represented by defect reaction. The excess cations or anions resulting from doping may be situated in part of the semiconductor lattice known as impurity defect. Defects are formed via physical processes. The defect processes for the formation of *n*-type or *p*-type semiconductor cancan be given by Eq. (1.6) and (1.7).

$$n\text{-type: SC} + \delta\text{D} \rightleftharpoons \text{D-SC} + \delta\text{e}^- \tag{1.6}$$

$$p\text{-type: SC} + \delta\text{A} \rightleftharpoons \text{A-SC} + \delta\text{h}^- \tag{1.7}$$

where SC is the semiconductor, δD and δA respresent small excess of donor or acceptor. The defect processes for the formation of *n*-type and *p*-type semiconductor can be more clearly illustrated using band gap model in Fig. 1.3.

It would be seen from the Fig. 1.3 that in the formation of *n*-type semiconductor the impurity the donor supplies electrons to the conduction band. Conversely, the formation of *p*-type semiconductor involves the acceptance of electrons from the