PHOTOCATALYSIS

Dimitris I. Kondarides
Department of Chemical Engineering, University of Patras, Greece

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Summary

Photocatalysis is a rapidly developing field of research with a high potential for a wide range of industrial applications, which include mineralization of organic pollutants, disinfection of water and air, production of renewable fuels, and organic syntheses. This article is focusing on semiconductor-mediated photocatalysis, that is, processes occurring on semiconductor-fluid interfaces irradiated with photons of proper energy. The theory and background necessary to understand semiconductor photocatalysis is first discussed, with emphasis given on the electronic and optical properties of bulk and particulate semiconducting materials. This is followed by the discussion of the principles of semiconductor photocatalysis and the thermodynamic and kinetic aspects which determine photocatalytic performance. The various types of available photocatalysts are then presented along with issues related to quantum efficiency, response to visible light and photochemical stability. A number of methods of improving photocatalytic performance are then described. The most important types of photoreactor configurations irradiated by artificial or solar light are presented and their advantages and disadvantages are discussed. Finally, a selection of representative semiconductor-mediated photocatalytic processes is presented, mainly focusing on environmental and energy related applications.
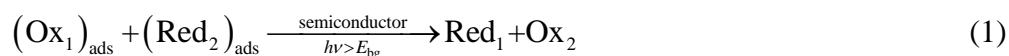
1. Introduction

The word "photocatalysis" is of Greek origin and composes of two parts: the prefix "photo" (*phos*: light) and the word "catalysis" (*katalyo*: brake apart, decompose). Although there is no consensus in the scientific community as to a proper definition of photocatalysis, the term can be generally used to describe a process in which light is used to activate a substance, the *photocatalyst*, which modifies the rate of a chemical

reaction without being involved itself in the chemical transformation. Thus, the main difference between a conventional thermal catalyst and a photocatalyst is that the former is activated by heat whereas the latter is activated by photons of appropriate energy. Photocatalytic reactions may occur homogeneously or heterogeneously, but *heterogeneous photocatalysis* is by far more intensively studied in recent years because of its potential use in a variety of environmental and energy-related applications as well as in organic syntheses. In heterogeneous photocatalysis, the reaction scheme implies the previous formation of an interface between a solid photocatalyst (metal or semiconductor) and a fluid containing the reactants and products of the reaction. Processes involving illuminated adsorbate-metal interfaces are generally categorized in the branch of *photochemistry*. Therefore, the term "heterogeneous photocatalysis" is mainly used in cases where a light-absorbing *semiconductor* photocatalyst is utilized, which is in contact with either a liquid or a gas phase. Here, we will restrict our attention to the description of semiconductor-mediated photocatalysis.

Semiconductors are particularly useful as photocatalysts because of a favorable combination of electronic structure, light absorption properties, charge transport characteristics and excited-state lifetimes. A semiconductor, by definition, is nonconductive in its undoped ground state because an energy gap, the *bandgap*, exists between the top of the filled valence band and the bottom of the vacant conduction band. Thus, electron transport between these bands must occur only with appreciable energy change. In semiconductor photocatalysis, excitation of an electron from the valence band to the conduction band is accomplished by absorption of a photon of energy equal to or higher than the bandgap energy of the semiconductor. This light-induced generation of an electron-hole pair is a prerequisite step in all semiconductor-mediated photocatalytic processes. Photogenerated species tend to recombine and dissipate energy as heat of photons, because the kinetic barrier for the electron-hole recombination process is low. However, conduction band electrons and valence band holes can be separated efficiently in the presence of an electric field, such as the one formed spontaneously in the space charge layer of a semiconductor-fluid or a semiconductor-metal interface. Thus, the lifetimes of photogenerated carriers increase and the possibility is offered to these species to exchange charge with substrates adsorbed on the photocatalyst surface and initiate chemical reactions.

Interfacial electron transfer, i.e., transfer of an electron to or from a substrate adsorbed onto the light-activated semiconductor is probably the most critical step in photocatalytic processes, and its efficiency determines to a large extent the ability of the semiconductor to serve as a photocatalyst for a given redox reaction. The efficiency of electron transfer reactions is, in turn, a function of the position of semiconductor's conduction and valence band-edges relative to the redox potentials of the adsorbed substrates. For a desired electron transfer reaction to occur, the potential of the electron acceptor species should be located below (more positive than) the conduction band of the semiconductor, whereas the potential of the electron donor species should be located above (more negative than) the valence band of the semiconductor. Interfacial electron transfer processes are then initiating subsequent (dark) redox reactions to yield the ultimate products. The latter catalytic reaction steps are not different from thermal catalysis, and similar principles will apply for a photocatalytic reaction as for a thermal catalytic reaction.

The overall scheme of a semiconductor-mediated photocatalytic reaction is often described by the following general equation:

$$\left(\text{Ox}_1\right)_{\text{ads}} + \left(\text{Red}_2\right)_{\text{ads}} \xrightarrow[h\nu > E_{\text{bg}}]{\text{semiconductor}} \text{Red}_1 + \text{Ox}_2 \tag{1}$$

The potential energy required for the chemical transformation to occur is overcome by the large amounts of "free energy" supplied with the ultra-violet or visible light quanta. Thus, in contrast to conventional thermal catalytic reactions, which usually rely on the application of high temperature and/or pressure, photocatalysis occurs under relatively mild (usually ambient) conditions with lower energy input. This is particularly true when the photocatalytic reaction is activated by solar light. An important characteristic of photocatalysts is that, in contrast to thermal catalysts, they can drive thermodynamically "uphill" reactions, i.e., reactions which involve transformations of substrates to products of higher potential energy. In this respect, a distinction is often made between "photocatalytic" and "photosynthetic" reactions, depending on whether the sign of the change in Gibbs free energy (ΔG^o) of reaction (1) is negative or positive, respectively. Examples of spontaneous, exergonic reactions ($\Delta G^o < 0$) include oxidation of organic pollutants present in the gas or liquid phase, whereas an example of a photosynthetic, endergonic reaction ($\Delta G^o > 0$) is the photocatalytic cleavage of water toward hydrogen (H_2) and oxygen (O_2).

A large variety of semiconducting materials, mainly metal oxides and chalcogenides, have been investigated with respect to their photocatalytic properties, but only few of them are considered to be effective photocatalysts. In general, wide-bandgap semiconductors, such as titanium dioxide (TiO_2), prove to be better photocatalysts than low-bandgap materials, such as cadmium sulfide (CdS), mainly due to the higher free energy of photogenerated charge carriers of the former and the inherently low chemical and photochemical stability of the latter. However, low bandgap semiconductors are better adapted to the solar spectrum, thereby offering the significant advantage of potential utilization of a continuous and readily available power supply, the sun. A considerable amount of effort has been made in recent years for the development of more efficient photocatalysts characterized by increased quantum efficiency and improved response to the visible spectral region. Promising results in this direction have been obtained with the use of several methods aiming at the modification of electronic and/or optical properties of semiconductors, including metal deposition, dye sensitization, doping with transition metals or non-metallic elements, use of composite semiconductor photocatalysts, etc.

The potential applications of heterogeneous photocatalysis depend strongly on the development of scaled-up reactor designs with increased efficiency. The major challenge in the design of a photocatalytic reactor is the efficient illumination of the catalyst and mass transfer optimization, especially in liquid phase reactions. Mass transfer limitations can be dealt with by the use of, for example, spinning disc reactors, monolithic reactors and microreactors, which have been proven to be much more efficient than conventional reactors. Photon transfer can be optimized with the use of optical fibers and light-emitting diodes (LEDs), but major breakthroughs in this field are

still lacking. Since the artificial generation of photons required for photocatalytic reactions is the most important source of operating costs in practical applications, a significant amount of research effort has been directed toward the development of solar photoreactors. Among the various types of solar reactor configurations evaluated so far, compound parabolic collectors are the most promising, and have been successfully scaled-up for applications related to wastewater treatment and water cleaning and disinfection.

Semiconductor photocatalysis is currently one of the most active interdisciplinary research areas, and has been investigated from the standpoint of catalysis, photochemistry, electrochemistry, inorganic, organic, physical, polymer and environmental chemistry. As a result of numerous investigations in these fields, the fundamental processes of photocatalysis are now much better understood. The applicability of photocatalysis has been proven in laboratory scale for a great number of different processes ranging from water treatment and air cleaning to disinfection and anti-tumoral applications, and from production of fuels from water and atmospheric gases to selective organic synthesis and metal recovery. However, industrial applications still remain limited. The current lack of widespread industrial applications is mainly due to the low photocatalytic efficiency of semiconductor photocatalysts and the absence of efficient, large scale photoreactor configurations.

2. Electronic and Optical Properties of Semiconductors

This chapter is aimed to serve as an introduction to the theory and background necessary to discuss semiconductor photocatalysts. Emphasis is given to the electronic and optical properties of semiconductors, which are described with the use of the band model, and to the principles of junction formation at the semiconductor-metal and semiconductor-fluid interfaces.

2.1. Fundamental Concepts

The electronic characteristics of conductors, semiconductors, and insulators can be described according to the *band theory*. Because of the very large number of atoms that interact in a solid material, the corresponding energy levels are so closely spaced that they form bands. Each band has a different energy, and the electrons fill these bands from the lowest energy to the highest, similar to the way that electrons occupy the orbitals in a single atom. The highest energy filled band, which is analogous to the highest occupied molecular orbital (HOMO) in a molecule, is called the valence band (VB). The next higher band, which is analogous to the lowest unoccupied molecular orbital (LUMO) in a molecule, is called the conduction band (CB). The VB and the CB are separated by an energy gap, the *bandgap* (E_{bg}). The filling of bands in a solid and the size of the bandgap determine if a material is a conductor, a semiconductor, or an insulator (see Figure 1). In general, for electrons to flow in a solid under the application of an electric field, they must be in a partially filled band or have access to a nearby empty band. In an electrical insulator, there is no possibility for electron flow, because the valence band is completely filled with electrons, and the conduction band is too far away in energy to be accessed by these electrons. In conductors like metals the valence band overlaps the conduction band. Thus, the electrons can access empty areas within

the valence band and move freely across all atoms that make up the solid. Finally a semiconductor is a special case in which the band gap is small enough (generally less than 4 eV) that it can be bridged by either heat or light, because these stimuli promote electrons from the valence band to the conduction band.
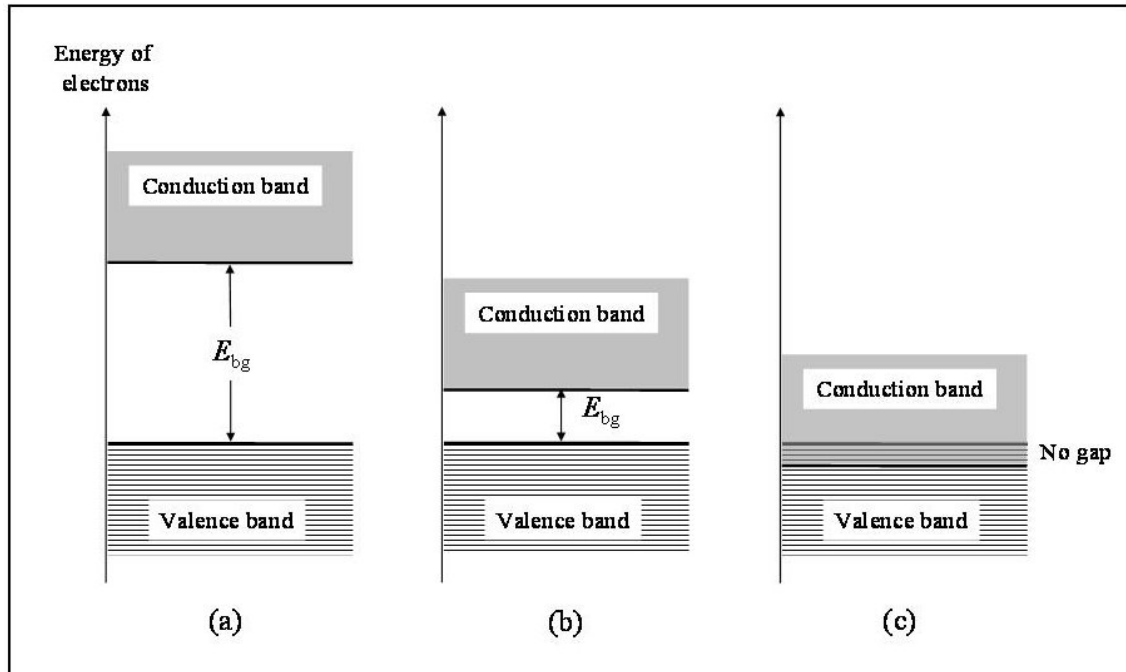

Figure 1. Energy bands in solids: (a) insulator; (b) semiconductor; (c) conductor.

Semiconductors are mainly classified into two categories: *intrinsic* and *extrinsic*. An intrinsic semiconductor is one, which is pure enough that impurities do not appreciably affect its electrical behavior. Elemental (e.g. Si, Ge) and compound (e.g. InSb, GaAs, SiC) semiconductors can be intrinsic semiconductors and possess poor conductivity. At a temperature of absolute zero (0 K) there are no charge carriers in an intrinsic semiconductor and therefore the material behaves as an insulator. In energy band terms, the CB is completely empty of electrons and the VB is fully occupied by the valence electrons. At a finite temperature, a valence band electron (e^-) may be thermally excited into the CB, leaving behind an unoccupied state in the valence band. This unoccupied state, which can be thought of as a second carrier of positive charge, is called a hole (h^+). Electrons and holes flow in opposite directions in the presence of an electric field but contribute to current in the same direction since they are oppositely charged. Holes and electrons created in this way are known as *intrinsic charge carriers*. In intrinsic semiconductors, for each and every electron in CB, there exists a corresponding hole (the empty state) in VB. Therefore, the electron concentration is equal to the hole concentration and this concentration is called the *intrinsic carrier concentration*, denoted as n_i.

An extrinsic semiconductor can be formed by addition of impurity atoms into the crystal of an intrinsic semiconductor, in a process known as *doping*. Doping results in a change of the relative concentrations of electrons and holes in the material in a manner, which

depends on the kind and concentration of the dopant atom. It should be noted that, although the number of free electron or hole concentration changes, a doped semiconductor is electrically neutral. Chemical impurities that contribute conduction electrons are called *donor impurities* or *donors*. Semiconductors doped with donors are called *n*-type semiconductors (*n* stands for negative). For example silicon, which belongs to group IV of the periodic table, has four valence electrons. When elements belonging to group V (e.g. As, P, Sb) are incorporated into a Si crystal, each dopant atom contributes an additional electron to the crystal thereby increasing its ability to conduct electricity. Impurity atoms that take away an electron from the semiconductor are called *acceptor impurities* or *acceptors* and result in the formation of *p*-type semiconductors (*p* stands for positive). For instance, when a group III element (e.g. B, Al, In, Ga) is incorporated into the crystal structure of silicon, the dopant atom has an insufficient number of bonds to share with the surrounding Si atoms. One of the silicon atoms has a vacancy for an electron and a hole is created, which contributes to the conduction process at all temperatures.

In an *n*-type semiconductor, electrons are the *majority carriers* and the electron concentration, *n*, is equal to the donor impurity concentration. Holes are *minority carriers* in *n*-type semiconductors. The opposite is true for *p*-type semiconductors, where holes are the majority carriers and their concentration, *p*, is equal to the acceptor impurity concentration. Electrons are minority carriers in *p*-type semiconductors.

2.2. The Electron Structure of Semiconductors

2.2.1. The Fermi Energy Level

An important parameter in the band theory is the *Fermi level*, E_F. Electrons in a solid are distributed in available energy states following the *Fermi-Dirac statistics*, which describes the probability that a given available energy level (E) will be occupied at a given temperature (T). The Fermi energy level is defined as the energy at which the probability of occupancy is equal to 0.5 and is related to the number of electrons in the system. Assuming that the number of electrons remains constant with temperature, then E_F also does not change with temperature. The Fermi level of intrinsic semiconductors is located midway between the conduction and valence bands to represent the equal statistical probability of finding a charge carrier in either of these two energy bands (see Figure 2).
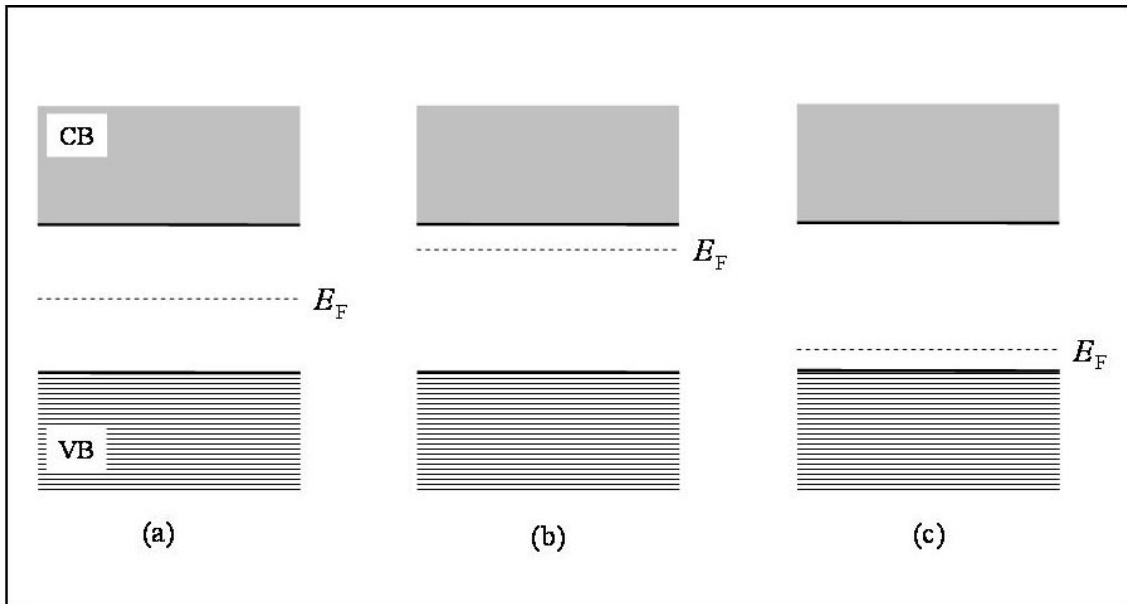
Figure 2. Position of Fermi level relative to VB and CB for (a) intrinsic, (b) *n*-type and (c) *p*-type semiconductors.

By doping an intrinsic semiconductor with donor impurities, the probability of encountering free electrons is increased and therefore the Fermi level shifts closer to the conduction band. By doping an intrinsic semiconductor with acceptor impurities, the probability of encountering free holes is increased, and therefore the Fermi level shifts closer to the valence band.

2.2.2. Energy Bands and Energy Levels

The electronic structure of a semiconductor material is usually represented with a band diagram, which plots the energy bands and energy levels versus position, x (see Figure 3). The energy states in the VB and CB of a semiconductor exist in an almost continuum, both in the "vertical" energy scale and in the "horizontal" spatial dimension. The upper edge of the valence band is denoted as E_{VB}, whereas the lower edge of the conduction band is denoted as E_{CB}. In solid state physics, the vacuum level is taken as the zero energy reference.

Figure 3. The electronic energy level diagram for a semiconductor.

The energy binding the electrons inside the semiconductor (and any other solid) corresponds to the electrochemical potential of the electrons, $\tilde{\mu}_e$. The condition of thermodynamic equilibrium requires that $\tilde{\mu}_e$ should be the same throughout the solid. The Fermi level is located inside the band gap and the Fermi energy is equal to the electrochemical potential of the semiconductor:

$$E_F = \tilde{\mu}_e \tag{2}$$

The work function of the semiconductor, Φ_{SC}, is defined as the difference between the Fermi level and the electrostatic (or outer) potential, Ψ, right out of the semiconductor surface:

$$\Phi_{SC} = -\tilde{\mu}_e - e\Psi \tag{3}$$

The work function, which incorporates the contribution of a term related to the bulk and a term related to the surface, represents the work needed to move an electron from the solid and place it at a distance x from the surface where the classical image-force potential, $-e^2/4x$, is just negligible. A distance of 10^{-4} cm is generally sufficient to meet this requirement.

Another important parameter is the electron affinity, χ_{SC}, which is defined as the difference between the edge of the conduction band and the electrostatic potential just outside the semiconductor:

$$\chi_{SC} = -E_{CB} - e\Psi \tag{4}$$

The electron affinity is a critical surface parameter that does not depend on the nature and concentration of dopants in a semiconductor.

2.2.3. Surface Versus Bulk Properties

The termination of the periodic structure of a semiconductor at its free surface eliminates its symmetry in the direction perpendicular to the surface and results in the formation of surface-localized electronic states *within* the semiconductor bandgap (see Figure 4). These states affect the electronic properties of the surface and may play an important role in the interaction with adsorbed species. Surface states can be introduced by (i) the presence of "dangling bonds", i.e., surface atoms with no upper atom to bind to; (ii) surface reconstruction or relaxation, i.e., a change in the position and/or chemical bonding configuration of surface atoms, which minimizes the surface energy, (iii) structural defects of the surface, i.e., steps and kinks; (iv) impurity atoms adsorbed on the surface; (v) bonding between the surface atoms and atoms of the new phase, etc. These energy levels, which are located in the forbidden gap region, are of special importance with regard to the optical properties of semiconductor photocatalysts.

The appearance of surface-localized states induces charge transfer between bulk and surface in order to establish thermal equilibrium between the two. Therefore, the carrier density in the vicinity of the surface deviates from its equilibrium value and results in the development of a non-neutral region (with a non-zero electric field) in the semiconductor bulk. This region is usually referred to as the surface *space charge region* (SCR). The bulk properties of pure semiconductors are recovered beyond a few atomic layers inside the crystal. However, in the case of doped semiconductors the presence of surface states leads to the formation of a SCR that can extend up to several thousand angstroms inside the solid. The electrostatic potential, V_s, produced by the space charge region causes a modification in the band structure near the surface, which is known as *band bending* (see Figure 4). By definition, the energy band is lower the

higher the electrical potential is, so a positive V_S corresponds to downward-bent bands. For *n*-type semiconductors, where electrons from the donor levels close to the surface region are transferred to the surface states, the bands rise up at the surface (see Figure 4). In a *p*-type semiconductor, the bands bend downward, since electrons are transferred from the surface states to the acceptor levels.
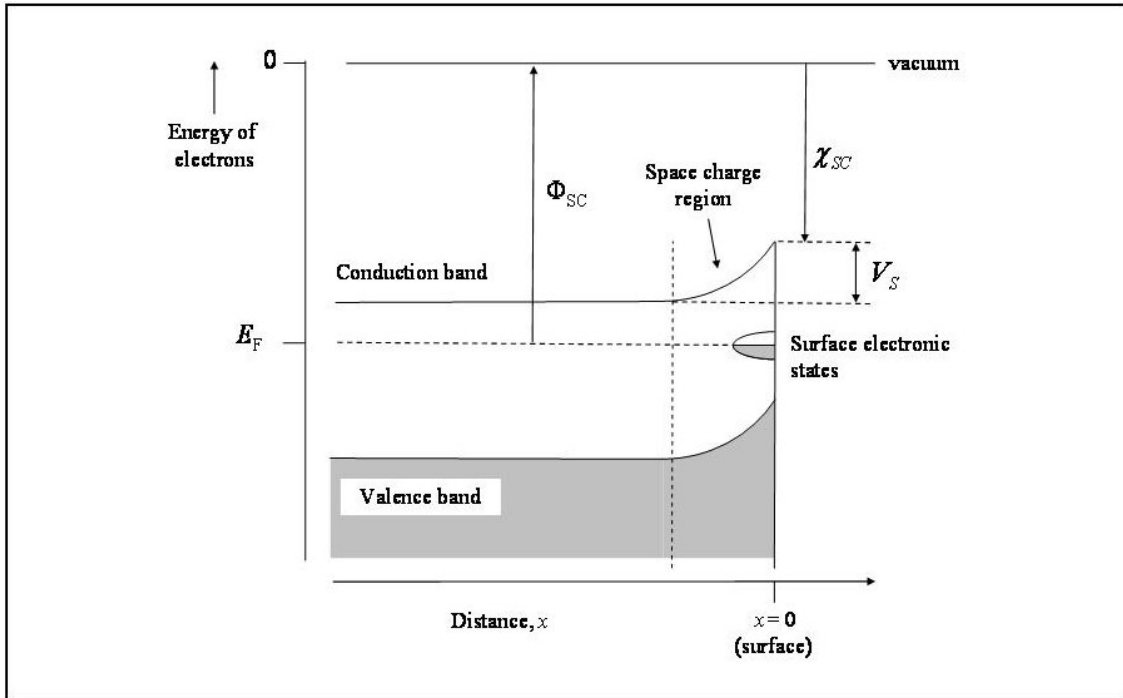

Figure 4. Schematic representation of the band bending for an *n*-type semiconductor surface. [Redrawn from "Heterogeneous Photocatalysis", M. Schiavello (Ed.), Chapter 2: A. Atrei and G. Rovida "Surface Versus Bulk Properties", John Wiley & Sons Ltd, 1997, England. With permission from Wiley-Blackwell, UK].

An effect of surface electronic states and band bending is that the work function of a doped semiconductor is nearly independent from the dopant concentration. Doping of a semiconductor with a donor impurity raises the Fermi level and this should result in a decrease of the work function. In fact, this effect is cancelled by the increase in the energy spent by an escaping electron to cross the space charge region and the work function is nearly independent from the dopant concentration. This phenomenon is known as *pinning* of the Fermi level for doped semiconductors.

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Bibliography

Beydoun D., Amal R., Low G. and McEvoy, S. (1999). Role of nanoparticles in photocatalysis. *Journal of Nanoparticle Research* 1, 439-458. [This review paper provides a detailed look at the unique properties of nanoparticles and their relation to photocatalytic properties. Also covered is the utilization of nanoparticles in doped, coupled, capped, sensitized and organic-inorganic nanocomposite semiconductor systems for the development of materials with enhanced photocatalytic properties].

Carp O., Huisman C.L. and Reller A. (2004). Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry* 32, 33-177. [This article provides a comprehensive review of photoinduced phenomena taking place over irradiated TiO_2 surfaces and their applications in solar cells to generate electricity, in chemical processes to create or degrade specific compounds and also in super-hydrophilicity].

Demeestere K., Dewolf J. and van Langenhove, H. (2007). Heterogeneous photocatalysis as an advanced oxidation process for the abatement of chlorinated, monocyclic aromatic and sulfurous volatile organic compounds in air: State of the art. *Critical Reviews in Environmental Science and Technology*, 37:6, 489-538. [This review focuses on both fundamentals and applicability of heterogeneous photocatalysis for the degradation of volatile organic compounds (VOC) in air].

Grätzel, M. (Editor) (1983). *Energy resources through photochemistry and catalysis*, Academic Press Inc, New York. [This book provides a detailed and in-depth presentation of photocatalytic processes related to energy-conversion, with emphasis given on photocleavage of water, reduction of carbon dioxide and fixation of nitrogen. Fundamental aspects related to light-induced redox reactions, reaction dynamics in organized assemblies such as micelles, colloidal metals, or semiconductors, and strategies for molecular engineering of artificial photosynthetic devices are also discussed].

Herrmann, J.-M. (2005). Heterogeneous photocatalysis: state of the art and present applications. *Topics in Catalysis* 34, 49-65. [This review paper presents the basic fundamental principles of photocatalysis and discusses the effects of the main operating parameters that govern the kinetics of photocatalytic reactions. The main fields of application of photocatalytic processes are presented along with some examples of solar photoreactor configurations].

Malato Rodríguez S., Blanco Gálvez J., Maldonato Rubio M.I., Fernández Ibáñez P., Alarcón Padilla D., Collares Pereira M., Farinha Mendez J. and Correia de Oliveira J. (2004). Engineering of solar photocatalytic collectors. *Solar Energy* 77, 513-524. [This paper describes the different collectors used in solar photocatalysis for wastewater treatment and the main advantages and disadvantages of each].

Robertson, P.K.J., Bahnemann, D.W., Robertson, J.M.C. and Wood, F. (2005). Photocatalytic detoxification of water and air. Editor: Hutzinger, O. *Handbook of Environmental Chemistry* (2005), Vol. 2, Part M, 367-423. Publisher: Springer, Berlin, Germany. [This chapter provides a review for the use of semiconductor photocatalysis for treatment of water and air. The fundamental processes involved in the technique are discussed and a range of applications of water and air treatment are described with examples of mechanistic pathways. Examples of large-scale water treatment applications are also discussed].

Schiavello, M. (Editor) (1997). *Heterogeneous photocatalysis*. Wiley Series in Photoscience and Photoengineering, Vol. 3. John Wiley & Sons Ltd. [This book outlines the fundamental principles of heterogeneous photocatalysis and presents a number of case studies which illustrate how these principles can be applied to engineering problems].

Serpone, M. and Pelizzetti, E. (Editors) (1989). *Photocatalysis: Fundamentals and applications*. John Wiley & Sons, Inc. [This book covers all aspects of photocatalysis, from interactions of light and matter and the theory of semiconductors to surface science of catalysis and photo-reactions at gas-solid and liquid-solid interfaces. Photocatalysis in both homogeneous and heterogeneous phases is treated, along with photoelectrocatalysis and photocatalysis in organized assemblies. A section is devoted to applications to energy production and environmental issues].

Biographical Sketch

Dimitris I. Kondarides is an Assistant Professor at the Department of Chemical Engineering of the University of Patras, Greece. He received his diploma in Chemistry in 1987 and his Ph.D. in Chemical Engineering in 1993 from the University of Patras. He was a postdoctoral fellow at the University of Tokyo from 1993 to 1994. From 1996 to 2001 he worked as a researcher at the Institute of Chemical Engineering (ICEHT/FORTH) and the Department of Chemical Engineering in Patras. In 2001 he became a Lecturer and in 2006 an Assistant Professor. His domains of professional interests are heterogeneous catalysis and photocatalysis, with emphasis given in environmental and energy-related applications.