Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results

Amy L. Linsebigler, Guangquan Lu, and John T. Yates, Jr.*
Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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1. Introduction

In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes.¹ This event marked the beginning of a new era in heterogeneous photocatalysis. Since then, research efforts in understanding the fundamental processes and in enhancing the photocatalytic efficiency of TiO₂ have come from extensive research performed by chemists, physicists, and chemical engineers. Such studies are often related to energy renewal and energy storage.²⁻⁶ In recent years, applications to environmental cleanup have been one of the most active areas in heterogeneous photocatalysis. This is inspired by the potential application of TiO₂-based photocatalysts for the total destruction of organic compounds in polluted air and wastewaters.⁷⁻⁸

In a heterogeneous photocatalysis system, photoinduced molecular transformations or reactions take place at the surface of a catalyst. Depending on where the initial excitation occurs, photocatalysis can be generally divided into two classes of processes. When the initial photoexcitation occurs in an adsorbate molecule which then interacts with the ground state catalyst substrate, the process is referred to as a catalyzed photoreaction. When the initial photo-
Amy Linsebigler received her B.S. degree in Chemistry from Seton Hill College in 1989. She is currently completing her Ph.D. in Chemistry at the University of Pittsburgh under the direction of Professor John T. Yates, Jr. During her doctoral studies she has examined several technologically important surface science systems. Her research includes the chemical reactivity of environmentally important adsorbates on metal surfaces, electronic modification of metal surfaces with thin metal films, and currently, the molecular level photochemistry and thermal chemistry of small probe molecules on metal oxide single-crystal surfaces.

Guangquan Lu was born on July 24, 1965, in Shandong, the People's Republic of China. He received his B.S. in Chemistry from Shandong University in 1985, and his Ph.D. in Chemistry from the University of California at San Diego in 1992. His primary research interests are the kinetics and dynamics of thermal and photochemical processes on semiconductor surfaces. He has been involved in a broad range of research projects including the surface characterizations of SiGe chemical vapor depositions, the surface chemistry of photocatalytic reactions on TiO₂, and the surface and interface characterizations of advanced electronic materials processing. He is the recipient of the CGP scholarship from the Chinese Education Commission (1985), the American Vacuum Society Student Prize (1990), and the Russell and Sigurd Varian Fellow Award (1990).

excitation takes place in the catalyst substrate and the photoexcited catalyst then transfers an electron or energy into a ground state molecule, the process is referred to as a sensitized photoreaction. The initial excitation of the system is followed by subsequent electron transfer and/or energy transfer. It is the subsequent deexcitation processes (via electron transfer or energy transfer) that leads to chemical reactions in the heterogeneous photocatalysis process. By using the electronic population changes in the molecular orbitals, Figure 1.1 schematically illustrates the different interactions between one reactive center in the excited state and another reactive center in the ground state. A reactive center can be a molecule or a surface reactive site.

Professor John T. Yates, Jr. began his research in surface chemistry as a graduate student at MIT. He continued this work from 1963 to 1982 at the National Bureau of Standards. In 1982 he founded the Surface Science Center at the University of Pittsburgh where he was appointed R.K. Mellon Professor. He now holds a joint appointment in the Departments of Chemistry and Physics. Work on metallic, semiconducting, and insulator surfaces is now underway using modern surface measurement techniques. His work with students and postdoctorals is focused on the use of electronic excitation to probe surface phenomena as well as the use of a range of surface vibrational spectroscopies and other methods for understanding surface processes.

**Figure 1.1.** Electron transfer and energy transfer processes.

An electron transfer process is a one-electron reaction in which an electron jumps from an occupied orbital of the donor reactant to the empty orbital of the acceptor reactant. The initial excitation may take place in either the donor molecule (\(D \rightarrow D^*\)) or the acceptor molecule (\(A \rightarrow A^*\)). The electron transfer process requires the overlap between the occupied donor orbital and the acceptor orbital which may be empty or half-filled. The electron transfer results in an ion pair of the donor cation (\(D^+\)) and the acceptor anion (\(A^-\)).

An energy transfer process takes place by electron exchange or dipole–dipole resonant coupling. These two processes operate through two fundamentally different mechanisms. Electron exchange occurs by two independent one-electron transfer steps—one in each direction. Both electron transfer and electron
exchange require orbital overlap between the interacting centers. When both processes are thermodynamically allowed, electron transfer predominates since the electron exchange process requires simultaneous overlap of two orbital pairs, whereas only one such overlap is necessary for electron transfer. Dipole–dipole coupling occurs by a Coulombic resonance interaction in which the oscillating dipole of an excited state molecule is coupled with the induced dipole in a ground state quencher molecule. This coupling process does not require effective orbital overlap between the two interacting centers and can operate over a distance range from less than 10 Å to as large as 100 Å.  

There exists a vast body of literature dealing with the electron transfer and energy transfer processes in photocatalytic reactions. A detailed description of these processes is beyond the scope of this review. Several excellent review articles and books already exist. Here, we tend to focus on interfacial electron transfer will be reviewed. Interfacial electron transfer occurs by a Coulombic resonance interaction in which the oscillating dipole of an excited state molecule is coupled with the induced dipole in a ground state quencher molecule. This coupling process does not require effective orbital overlap between the two interacting centers and can operate over a distance range from less than 10 Å to as large as 100 Å.  

The efficiency of the photoinduced chemistry is controlled by the system’s light absorption characteristics. In this section, we want to examine the overall factors that control the light absorption intensity by the molecule or by the substrate. The electronic interaction between the adsorbate molecule and the catalyst substrate will then be discussed and modified at metal–semiconductor interfaces. Some concluding remarks and future research directions will be given in the final section.

2. Electronic Processes in Photocatalysis

2.1. Molecular Electronic Excitation

2.1.1. Molecular Spectroscopy and Photochemistry

Photocatalysis processes involve the initial absorption of photons by a molecule or the substrate to produce highly reactive electronically excited states. The efficiency of the photoinduced chemistry is controlled by the system’s light absorption characteristics. In this section, we want to examine the factors that control the light absorption intensity by the molecule or by the substrate. We will first discuss the electronic excitation of a molecule upon photon absorption. The band-gap excitation of the semiconductor substrate will then be discussed and interfacial electron transfer will be reviewed.

Molecular electronic spectroscopy is a useful tool to determine where photochemistry may potentially occur. Most importantly, we can determine what photon energy will most likely induce an electronic transition in a molecule based on whether the transition dipole moment will be zero for a transition from the initial state “i” to the final state “f”. A transition that is forbidden by the selection rules is expected to have no absorption intensity (μif = 0), and it will therefore be unlikely to cause photochemical conversions which involve the excitation of such a transition.

The probability of an electronic transition can be calculated, using quantum mechanics perturbation theory, as being proportional to the square of the amplitude of the radiation field, E0, and the square of the transition dipole moment, |μif|  

\[ P \propto E_0^2 |μ_{if}|^2 \]  

Here |μif| = ⟨ψf|μ|ψi⟩ is the transition dipole moment for an electronic excitation process from the initial state |ψi⟩ to the final state |ψf⟩. While the radiation field can be controlled by varying the light intensity, the transition dipole moment is an intrinsic property of the molecular structure.

According to the Born–Oppenheimer approximation, the molecular wave function Ψ can be expressed as the products of the electronic spatial wave function ϕ, the electronic spin wave function ω, and the nuclear wave function Φ.  

\[ \Psi = ϕ \cdot ω \cdot Φ \]  

Now the transition dipole moment may be regarded as the product of the electronic transition moment, the electron spin wave function overlap, and the nuclear wave function overlap. The transition dipole moment, μif, will be zero if any of these three contributions become zero. This gives the selection rules for an electronic excitation process.

The electronic transition moment term ⟨ψf|μ|ψi⟩ depends on the nature of the electron distributions in the initial and final electronic spatial wave functions. By examining the overall symmetry property of the spatial wave functions, one can easily determine if this integral is zero. When this term is zero, the transition dipole moment μif is zero. Then the transition is a symmetry-forbidden transition.

The overlap integral of the spin wave functions ⟨ωf|ωi⟩ can be evaluated using the orthogonal property of the electron spin wave functions, that is,  

\[ ⟨α|α⟩ = ⟨β|β⟩ = 1 \quad ⟨α|β⟩ = ⟨β|α⟩ = 0 \]  

Here α and β correspond to the only two spin configurations, spin-up (α) and spin-down (β). The electron spin functions maintain their orthogonality and normalization properties even when the electrons under consideration are described by different spatial wave functions. Using these properties, we can easily derive that the original spin orientation ωi must be preserved in the final excited state in order to keep the term ⟨ωf|ωi⟩ non-zero. Therefore, singlet–singlet and triplet–triplet transitions are spin-forbidden, while a singlet–triplet transition is spin-allowed. Exceptions to this rule are often found among complex organic molecules containing heavy atoms (such as Br or I). Spin–orbit coupling induces weakly allowed singlet–triplet transitions in these systems.
Although the selection rules are often broken in the real world due to the simplicity of the molecular quantum mechanics formulations used to develop these selection rules, it is certainly true that a transition predicted to be forbidden will be very weak. These principles provide for us a set of generalities that we can use to understand patterns in experimental photochemistry. The excitation of a weak transition will not effectively induce a photochemical reaction in the sense that few of the delivered photons will actually be absorbed (low cross section). However, we must keep in mind that the reaction itself will be very efficient if each absorbed photon can lead to the formation of a product molecule (high quantum yield). Thus, molecules with low absorption intensities are not necessarily poor photochemical reagents. The photochemical efficiency of an excitation will also be determined by which deexcitation channel is dominant, as discussed below.

2.1.2. Molecular Excitation and Deexcitation Events

The allowable excitation and deexcitation processes for a molecule are given in the energy level diagram in Figure 2.2. The ground state singlet energy level of the molecule is represented by $S_0$ and illustrates the energy of the molecule at room temperature in solution. The ground vibrational states for the three excited electronic states shown in Figure 2.2 for the molecule are represented as $S_1$ for the singlet states and $T_1$ for the triplet state. The triplet excited state for the molecule is less energetic than the singlet excited state of the molecule. The respective energy levels of the excited states of the molecule are important when dealing with the photosensitization of semiconductors via dye molecule excitation. Numerous vibrational energy levels associated with the electronic energy levels exist but are not shown to simplify the figure. Absorption of radiation results in the excitation of the molecule from the ground state to one of the excited singlet states. The excitation to the second singlet state $S_2$ (requiring a shorter wavelength than excitation to $S_1$) is illustrated in Figure 2.2. The selection rules for an electronic excitation process imply that direct photoexcitation from the singlet ground state to the triplet excited state is spin forbidden ($\langle S_0 | S_1 \rangle = 0$). The absorption

Figure 2.1. Vibronic transitions in a diatomic molecule.

Figure 2.2. Excitation and deexcitation processes in a molecule.
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of a photon of radiation occurs very rapidly, on the order of $10^{-15}$ s.²⁴a Deexcitation events are much slower.

The deexcitation of the excited molecule favors the route which will minimize the lifetime of the excited state. Whether it occurs via emission of radiation such as fluorescence or phosphorescence, or a radiationless decay, indicated in Figure 2.2 as curvy lines, depends upon the competition between different decay channels. The lifetime of the excited state for fluorescence emission is $10^{-9}$ to $10^{-5}$ s.²⁴a

After the excitation of a molecule from the ground state to a higher nondissociative excited state occurs, radiationless internal conversion transitions to the lower excited states usually take place before any radiative emission processes.²⁵ The conversion is observed when the upper electronic energy levels are close together and the vibrational energy levels overlap. The transition process from $S₂$ to $S₁$ is isoenergetic through overlay between vibrational levels. Once the transition occurs, the molecule undergoes vibrational relaxations to the ground vibrational state of the $S₁$ electronic excited state at a significant rate. Therefore, the $S₂$ to $S₁$ transition in Figure 2.2 represents a loss of energy for the internal conversion process. The time scale for internal conversion is $10^{-14}$ to $10^{-13}$ s.²⁴a Internal as well as external conversions can also occur from the lowest excited states $S₁$ and $T₁$ to the ground state $S₀$. External conversions are the result of energy transfer to solvent or solute molecules and are usually only from the lowest excited states. If overlapping vibrational energy levels exist, deactivation via internal conversion to the ground state can occur faster than that involved in fluorescence emission.

Figure 2.2 represents excitation to bound upper electronic states for the purpose of illustrating the various classes of electronic transitions which are possible. Other upper states may involve chemical changes such as dissociation and are not shown here.

Intersystem crossing is a process in which the spin of the excited electron is reversed and the electrons become unpaired. Intersystem crossing is illustrated in Figure 2.2 between the $S₁$ and $T₁$ excited states. This process is the result of vibrational states overlapping. The time required for such a process is in the range of $10^{-6}$ s.²⁴a Once intersystem crossing occurs from a singlet to a triplet excited state, the molecule undergoes deactivation by phosphorescence. The time scale for the radiative phosphorescence process is on the order of $10^{-5}$ to $10^{-3}$ s.²⁴a

Relaxation of the excited singlet and triplet states can also occur by decomposition of the excited species to form new chemical species. Such reactions include photoinduced fragmentation, intramolecular transformation, and intermolecular and interfacial electron or energy transfer. The photochemical reactions occur on a time scale of $10^{-12}$ to $10^{-9}$ s.²⁴b

2.2. Semiconductor Electronic Excitation

2.2.1. Band-Gap Photoexcitation

Unlike metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation in the solid. The void region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called the band gap. Once excitation occurs across the band gap there is a sufficient lifetime, in the nanosecond regime,²⁶ for the created electron–hole pair to undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact. If the semiconductor remains intact and the charge transfer to the adsorbed species is continuous and exothermic the process is termed heterogeneous photocatalysis.

The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron–hole pairs in the semiconductor particles. The enlarged section of Figure 2.3 shows the excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than

Figure 2.3. Schematic photoexcitation in a solid followed by deexcitation events.
the band gap of the semiconductor. Upon excitation, the fate of the separated electron and hole can follow several pathways. Figure 2.3 illustrates some of the deexcitation pathways for the electrons and holes.

The photoinduced electron transfer to adsorbed organic or inorganic species or to the solvent results from migration of electrons and holes to the semiconductor surface. The electron transfer process is more efficient if the species are preadsorbed on the surface.\(^\text{27}\) While at the surface the semiconductor can donate electrons to reduce an electron acceptor (usually oxygen in an aerated solution) (pathway C); in turn, a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (pathway D). The probability and rate of the charge transfer processes for electrons and holes depends upon the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbate species.

In competition with charge transfer to adsorbed species is electron and hole recombination. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle (pathway B) or on the surface (pathway A) with the release of heat. The process of back-donation after charge transfer from the adsorbed species to the semiconductor surface can occur but is not illustrated in Figure 2.3.

The efficiency of the photocatalytic process is measured as a quantum yield which is defined as the number of events occurring per photon absorbed. The ability to measure the actual absorbed light is very difficult in heterogeneous systems due to scattering of light by the semiconductor surface. It is usually assumed that all the light is absorbed and the efficiency is quoted as an apparent quantum yield. If several products are formed from the photocatalytic reaction then the efficiency is sometimes measured as the yield of a particular product.

To determine the efficiency or quantum yield, a combination of all the pathway probabilities for the electron and hole must be considered. The quantum yield for an ideal system, \(\phi\), given by the simple relationship:

\[
\phi \propto \frac{k_{\text{CT}}}{k_{\text{CT}} + k_R}
\]

is proportional to the rate of the charge transfer processes \((k_{\text{CT}})\) and inversely proportional to the sum of the charge transfer rate \((k_{\text{CT}})\) and the electron–hole recombination rate \((k_R)\) (bulk and surface). It is assumed that diffusion of the products into the solution occurs quickly without the reverse reaction of electrons recombining with donors and holes recombining with acceptors. Without recombination the quantum yield would take the ideal value of 1 for the photocatalytic process. In this case the rate of charge transfer would be dependent on the diffusion of charge carriers to the surface in the absence of excess surface charge. However, this is an idealization. In a real system recombination does occur and the concentration of electrons \((n_e)\) and holes \((p_h)\) at the surface is not equal.\(^\text{28}\) For example, charge carrier traps are used to promote the trapping of electrons and holes at the surface leading to a more efficient charge transfer process. For photooxidation processes on \(\text{TiO}_2\), \(n_e > p_h\), because the electron transfer process to molecular oxygen trapped at defect sites is relatively slow.\(^\text{28}\)

Obviously electron and hole recombination is detrimental to the efficiency of a semiconductor photocatalyst. Modifications to semiconductor surfaces such as addition of metals, dopants, or combinations with other semiconductors are beneficial in decreasing the electron and hole recombination rate and thereby increasing the quantum yield of the photocatalytic process. Such semiconductor modifications will be discussed in detail in section 4 later in the review.

2.2.2. Band-Edge Positions

The ability of a semiconductor to undergo photoinduced electron transfer to adsorbed species on its surface is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbate. The relevant potential level of the acceptor species is thermodynamically required to be below (more positive than) the conduction band potential of the semiconductor. The potential level of the donor needs to be above (more negative than) the valence band position of the semiconductor in order to donate an electron to the vacant hole.

The band edge positions of several semiconductors are presented in Figure 2.4. The internal energy scale is given on the left for comparison to the vacuum level and on the right for comparison to normal hydrogen electrode (NHE). The positions are derived from the flat band potentials in a contact solution of aqueous electrolyte at \(\text{pH} = 1\). The \(\text{pH}\) of the electrolyte solution influences the band edge positions of the various semiconductors compared to the redox potentials for the adsorbate.

2.2.3. Charge Carrier Trapping

Recombination of the photoexcited electron–hole pair needs to be retarded for an efficient charge
transfer process to occur on the photocatalyst surface. Charge carrier trapping would suppress recombination and increase the lifetime of the separated electron and hole to above a fraction of a nanosecond. In the preparation of colloidal and polycrystalline photocatalysts, ideal crystal lattices of the semiconductors are not produced. Instead, surface and bulk irregularities naturally occur during the preparation process. The irregularities are associated with surface electron states which differ in their energy from the bands present in the bulk semiconductor. The electron states serve as charge carrier traps and help suppress the recombination of electrons and holes.

The nature of surface defect sites depends on the method of chemical preparation. As a specific example of the role of surface traps, CdS colloids produced by adding H₂S to a cadmium salt solution possess surface defect sites which promote radiationless recombination of charge carriers. The radiationless recombination process dominates in this semiconductor system. The fluorescence spectrum of this colloidal suspension exhibits only a very weak red fluorescence peak at a photon energy 0.4 eV below the absorption threshold. The decrease in energy is due to the trapping of charge carriers on the surface at energy levels below the conduction band edge. After modifying the surface by addition of excess Cd²⁺ ions and an adjustment in pH toward a basic solution, the maximum of fluorescence occurs at the absorption threshold (2.48 eV). The surface modification blocks defect trap sites which also promote radiationless recombination of charge carriers. The high quantum yield (50%) for fluorescence on the modified CdS is a result of electron–hole pair recombination across the bulk band gap.

A simplified illustration of available bulk and surface trapping states for a photogenerated electron in a semiconductor is shown in Figure 2.5. In this illustration, the energy levels of the bulk and surface state traps fall within the band gap of the semiconductor. These surface and bulk states are localized. The charge carriers trapped in such states are localized to a particular site on the surface or in the bulk. The population of bulk and surface traps is dependent on the energy difference between the trap and the bottom of the conduction band and the decrease in entropy when the electron undergoes trapping. Experimentally, trapping of conduction band electrons generated by picosecond laser photolysis of colloidal TiO₂ has been observed. Time-resolved transient absorption of trapped electrons have demonstrated a lifetime in the nanosecond time range. The trapping of valence band holes required an average time of 250 ns. Electron paramagnetic resonance (EPR) spectroscopy experiments of illuminated colloidal TiO₂ at 4.2 K have shown the existence of trapped photogenerated electrons (to form Ti³⁺ defect sites) within the bulk of the semiconductor. Adsorbed oxygen on the TiO₂ surface scavenges the trapped electrons and inhibits the formation of Ti³⁺ sites. Trapped holes are also observed. The exact species associated with the trapped hole is undetermined, although O⁻, O₃⁻, and ·OH species are postulated to exist in various cases.

Further illustrations of the nature and role of defect sites are given in sections 3.1 and 3.2.

2.2.4. Quantum Size Effects

Size quantization effects for metals and semiconductors have recently been a subject of great interest, and several reviews are available. Quantum size effects (QSE) occur for semiconductor particles (Q-particles) on the order of 10–100 Å in size. The anomalies arise when the size of the semiconductor particles become comparable to the de Broglie wavelength of the charge carriers in the semiconductor. The range of size for particles experiencing QSE is therefore dependent on the effective mass for the Q-particle semiconductor. The electron and hole produced in Q-particles are confined in a potential well of small geometrical dimensions. The electron and hole do not experience the electronic delocalization present in a bulk semiconductor possessing a conduction band and a valence band. Instead, the confinement produces a quantization of discrete electronic states and increases the effective band gap of the semiconductor. Such effects can change the color of the material (due to the altered optical absorption maxima) and the photocatalytic properties.

Recent advances in the ability to synthesize cluster particles allows the study of size-dependent anomalies compared to the bulk properties. ZnO, CdS, and PbS are the Q-particles studied in the most detail both experimentally and theoretically. Figure 2.6 illustrates the increase in effective band gap for CdS when the size of the particles is decreased from d > 100 Å, signifying the dimensions of a bulk semiconductor, to d ~ 26 Å where significant quantum size effects occur for CdS. This
quantization and increase in effective band gap is observed experimentally as a blue shift in the absorption and emission spectra for CdS. The energy shift in the band gap, $\Delta E$, as a function of particle size can be predicted by the three dimensional confinement model based on the effective mass approximation:

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.786e^2}{eR} - 0.248E_{\text{RY}}$$  \hspace{1cm} (6)

where $R$ is the particle radius, $m_e^*$ and $m_h^*$ are the effective masses for the electrons and holes, $e$ is the dielectric constant, and $E_{\text{RY}}$ is the effective Rydberg energy given as $e^2/2e\hbar^2(1/m_e^* + 1/m_h^*)$. The equation is characterized by the first term which represents the energy of localization, the second term which represents the Coulombic attraction, and the third term which represents the correlation effect. $\Delta E$ gives the blue shift in the band gap of the particle:

$$E_{\text{TE}} = \Delta E + E_{g}^{\text{bulk}}$$  \hspace{1cm} (7)

and determines the transition energy (effective band gap), $E_{\text{TE}}$, for the particle.

The increase in effective band gap and consequently the blue shift in the absorption threshold, can become quite dramatic for bulk semiconductors with very small band gaps. The band gap for PbS ($E_g^{\text{bulk}} = 0.4$ eV) can actually be increased by a factor of 6 when the particle size is decreased from 150 to 13 Å. When the Q-particle sizes are less than 13 Å, discrete absorption bands are observed in the absorption spectrum for PbS. A theoretical treatment for PbS has shown that the simple confinement model using the effective mass approximations cannot reproduce the experimental results. Other theoretical treatments have also been developed to fit the experimental data for the very small diameter particles <15 Å. While photocatalyst particles have not reached Q-particle sizes yet, it can be expected that this may happen in the future as new materials are produced.

### 2.2.5 Band Bending and Formation of Schottky Barrier

Contact between a semiconductor and another phase (i.e. liquid, gas, or metal) generally involves a redistribution of electric charges and the formation of a double layer. The transfer of mobile charge carriers between the semiconductor and the contact phase, or the trapping of charge carriers at surface states at the interface, produces a space charge layer. For semiconductor–gas phase interactions, an n-type semiconductor such as TiO$_2$ can have surface states available for electron trapping. The surface region will become negatively charged. To preserve electroneutrality a positive space charge layer develops just within the semiconductor causing a shift in electrostatic potential and a bending of bands upward toward the surface.

Figure 2.7 illustrates the space charge layers produced from the mobility of charge across a semiconductor–solution interface for an n-type semiconductor. Part a of Figure 2.7 shows the flat band potential diagram in the absence of a space charge layer. The semiconductor contains a uniform distribution of charge. The existence of a positive charge on the interface (part b) increases the majority carrier concentration of electrons near the surface within the region of the space charge layer. The space charge layer formed is called an accumulation layer. The bands of the semiconductor will bend down as one moves toward the surface as a result of the decrease of electron potential energy as one moves toward the positively charged outerlayer. When negative charges accumulate at the interface the majority electron carrier concentration is less than in the interior of the semiconductor (part c). The space charge layer formed is a depletion layer and the bands bend upward toward the surface. When the depletion of the majority charge carriers extends far into the semiconductor, the Fermi level can decrease below the intrinsic level, which is half way between the bottom of the conduction band and the top of the valence band. The surface region of the semiconductor appears to be p-type while the bulk still exhibits n-type behavior. This space charge layer is called an inversion layer (part d).

The semiconductor–metal system represents a good example illustrating space charge layers, band bending, and the formation of a Schottky barrier as shown in Figure 2.8. Electrically neutral and isolated from each other, the metal and the n-type semiconductor have different Fermi level positions. In the case to be discussed here, the metal has a higher work function ($\phi_m$) than the semiconductor ($\phi_s$). When the two materials are connected electrically, electron migration from the semiconductor to the metal occurs until the two Fermi levels are equal.
aligned as shown in Figure 2.8. The electrical contact has formed a space charge layer. The surface of the metal acquires an excess negative charge while the semiconductor exhibits an excess positive charge as a result of electron migration away from the barrier region. The bands of the semiconductor bend upward toward the surface, and the layer is said to be depleted. The barrier formed at the metal—semiconductor interface is called the Schottky barrier. The height of the barrier, $\phi_b$, is given by

$$\phi_b = \phi_m - E_x$$  \hspace{1cm} (8)

where $E_x$ is the electron affinity, measured from the conduction band edge to the vacuum level of the semiconductor. The diagram in Figure 2.8 illustrates an ideal metal—semiconductor contact, i.e. no surface states exist on the semiconductor, etc. The Schottky barrier produced at the metal—semiconductor interface can serve as an efficient electron trap preventing electron—hole recombination in photocatalysis as discussed in section 4.2.

### 2.3. Photoinduced Electron Transfer Processes on the Surface of Catalysts

In an electronically excited state, a molecule or semiconductor particle becomes highly reactive. Electron transfer occurs between molecules at the surface or between a surface site and an adsorbate molecule. Similar to the classification of photocatalysis, electron transfer processes can also be broadly divided into two general categories as shown in Figure 2.9, parts I and II. The categories involve either excitation of the adsorbate directly by the photon or excitation of the solid by the photon followed by excitation of the adsorbate.

For a catalyst substrate with no accessible energy levels for the adsorbate, such as SiO$_2$ and Al$_2$O$_3$, only a 2D environment is provided for the reactant molecules, and the solid does not participate in the photoinduced electronic process. Electron transfer occurs directly from the adsorbed donor molecule to the acceptor molecule as shown in Figure 2.9I, part A. When there are accessible energy levels in the substrate and there is strong electronic interaction between the substrate and the adsorbate, the electron transfer may be mediated by the substrate. An electron is transferred from the donor into a substrate level and then into the acceptor orbital, as shown in Figure 2.9I, part B. This scheme operates in the photosensitization of semiconductor particles by dye molecules, as will be discussed in section 4.4. An electron is injected from the excited state dye molecule into the semiconductor particle which then reduces another adsorbate molecule.

In Figure 2.9II, part C, the initial excitation takes place in the substrate. For a semiconductor, an electron is excited into the conduction band of the semiconductor, leaving a positively charged hole at the band edge of the valence band. An electron is transferred into the empty acceptor orbital from the catalyst conduction band. Simultaneously, an electron is donated from the filled donor orbital to recombine with the hole at the valence band edge. This case is generally seen in most photocatalysis processes on wide band-gap oxide semiconductor surfaces, and is the focus of the rest of this review. Figure 2.9I, part D shows a common excitation scheme observed for adsorbates on metals. When the metal is irradiated, a hot electron is generated at a level above the Fermi edge and this electron then tunnels into an empty level in the adsorbate molecule. Processes occurring by this type of electron transfer process have been reviewed recently.

The interfacial electron transfer process has been extensively investigated and the dynamics of such processes continue to attract intensive research effort. The rate constant for an interfacial electron transfer is found to be greater than $5 \times 10^{10}$ s$^{-1}$. The driving force for the heterogeneous electron transfer is the energy difference between the conduction band of the semiconductor and the reduction potential of the acceptor redox couple, $\Delta E = E_{cb} - E_A^{-}$.

### 3. Photocatalysis on TiO$_2$

#### 3.1. The Lattice and Electronic Structure of TiO$_2$

#### 3.1.1. The Lattice Structure of Rutile and Anatase

Two different crystal structures of TiO$_2$, rutile and anatase, are commonly used in photocatalysis, with anatase showing a higher photocatalytic activity. The structure of rutile and anatase can be described in terms of chains of TiO$_6$ octahedra. The two crystal structures differ by the distortion of each octahedron and by the assembly pattern of the octahedra chains. Figure 3.1 shows the unit cell structures of the rutile and anatase crystals. Each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2−}$ ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti–Ti distances in anatase are greater (3.79 and 3.04 Å vs 3.57 and 2.96 Å in rutile) whereas the Ti–O distances are shorter than in rutile (1.934 and 1.980 Å in anatase vs 1.949 and 1.980 Å in rutile). In the rutile structure each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in the anatase structure each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO$_2$, as indicated in Figure 3.1.

#### 3.1.2. Geometric and Electronic Structure of TiO$_2$ Single-Crystal Surfaces

The surface structure of rutile single crystals have been studied with the rutile (110) surface being most extensively investigated. Figure 3.2 shows the model structures for the TiO$_2$(110) surface. This surface is thermodynamically most stable. Other faces will reconstruct upon heating to high temperatures to produce (110) facets. The structure of three types of oxygen vacancy sites are also shown in the figure.
I. PHOTOREACTION – INITIAL EXCITATION OF ADSORBATE

A. Insulator

B. Semiconductor

II. PHOTOREACTION – INITIAL EXCITATION OF SOLID

C. Semiconductor or Insulator

D. Metal

Figure 2.9. (I) Catalyzed photoreaction, initial excitation of adsorbate, and (II) Sensitized photoreaction, initial excitation of solid.

The electronic structure of the nearly perfect TiO₂ surfaces is essentially identical to that of the bulk rutile TiO₂. Figure 3.3 shows the photoemission spectra from vacuum-fractured (110), (100), and (001) faces of rutile TiO₂. All three faces give spectra similar to that of the bulk. The intense peak at \( \sim 6 \) eV is due to electron emission from the O 2p orbitals. The small emission peak near the Fermi level is due to point defect oxygen vacancies. This feature is more clearly shown in Figure 3.4. Figure 3.4 shows the electronic band structure constructed from photoemission (UPS) and inverse photoemission (IPS) spectra for a slightly defective TiO₂(110) surface. The filled valence band at \( \sim 6 \) eV is composed of O 2p orbitals (as shown in the UPS spectrum) and the empty conduction band is composed of Ti 3d, 4s, and 4p orbitals. The Ti 3d orbitals dominate the lower portion of the conduction band. The weak emission at \( \sim 0.8 \) eV below the Fermi level is associated with the defect induced-Ti 3d-derived levels. This state can be eliminated by surface oxidation.

Few studies have been conducted on the structure of the anatase single crystal surfaces. A recent photoemission study by Sanjines et al. has shown that anatase TiO₂(101) and polycrystalline anatase thin films exhibit similar electronic photoemission.
behavior to that of rutile. A similar 0.8 eV emission feature was observed upon the introduction of Ti$^{3+}$ defect sites by sputtering or H$_2$ reduction.

### 3.2. Chemisorption Studies on TiO$_2$ Surfaces

The chemisorption properties on TiO$_2$ surfaces have been extensively studied. Particular interest has been given to the influence of defect sites on the chemisorptive behavior of the surface. Since these defect sites are also found as the active sites for photocatalytic processes, we will in this section briefly summarize the results of recent chemisorption studies and try to illustrate some of the common characteristics of the TiO$_2$ surfaces.

#### 3.2.1. Water Adsorption

Much of the interest in studying the interaction of water with TiO$_2$ surfaces was stimulated by the discovery of the photocatalytic splitting of water on TiO$_2$ electrodes. Efforts have been focused on what forms of water (molecular or dissociated) exist on the surface and what are the important parameters in controlling the adsorption behavior. Henrich et al. detected surface hydroxyl groups present after H$_2$O adsorption at 300 K on a slightly defective TiO$_2$(110) surface with photoemission (UPS). This result was confirmed in a synchrotron photoemission study by the Madey group. The amount of water dissociatively adsorbed at 300 K was well below one monolayer and the coverage of OH(a) was found to be independent of the coverage of surface oxygen vacancy defect sites. In fact, surface defect coverage was found to slightly increase during H$_2$O adsorption. On the basis of these results, it was proposed that an adsorbed H$_2$O molecule reacts with a bridging-oxygen atom to form two OH groups.
above 200 K. However, most of the adsorbed water desorbs molecularly between 170–180 K. The hydroxyls were not completely removed from the surface until 350–400 K.

A recent XPS and TPD study by Hugenschmidt et al. reported four different adsorption states for H2O on TiO2(110), a 500 K TPD peak due to surface hydroxyls bound to oxygen vacancies, a 375 K peak due to dissociated H2O, a 250–300 K feature due to molecular H2O adsorbed at Ti4+ sites, a 170 K desorption feature due to molecular H2O bound to bridging-oxygen anion sites, and a 160 K multilayer state. The assignments of the 250–300 K and the 170 K peaks are inconsistent with the results by the Madey group which attributed these two states to the dissociated and first monolayer water adsorption, respectively. A recent study by Lu et al. demonstrated that, in addition to the molecular and dissociative adsorption, water molecules can be reduced at the Ti3+ sites on the TiO2(110) surface to produce hydrogen gas. The oxygen atom in the water molecule is preferentially extracted by the substrate to fill the surface oxygen vacancies. This selective reduction process (as well as others) can be used to infer the relative coverage of oxygen vacancy defect sites.

The interaction of water with other single-crystal TiO2 surfaces as well as powdered TiO2 has also been investigated. Bustillo et al. and Lo et al. studied the thermal desorption of water from the TiO2(100) surface and reported dissociative adsorption of water. On powdered TiO2, three TPD peaks can be observed. A poorly resolved doublet at ~211 K was attributed to multilayer and monolayer adsorption. A 311 K desorption peak was assigned to a different form of molecularly adsorbed H2O, and a 568 K desorption was thought to arise from dissociatively adsorbed H2O. The production of hydrogen gas was also detected for H2O adsorption on reduced TiO2 powder, indicating that the reduction property is characteristic of the Ti3+ defect sites.

3.2.2. H2 Adsorption

Göpel et al. studied the adsorption of hydrogen on the TiO2(110) surface using temperature programmed desorption (TPD), electron paramagnetic resonance (ESR), and measurements of surface conductivity (∆σ) and work function (∆φ). The surface defect sites (oxygen vacancies) were found to act as electron donors and are the specific sites for H2 adsorption. Chemisorption of hydrogen at 300 K forms ionic titanium hydride bonds Ti4+H-, after H2 dissociative adsorption at the defect sites. This process involves the transfer of two electrons which before adsorption were attributed to one oxygen vacancy site (with two Ti3+ present). These two hydrogen atoms can easily recombine during subsequent thermal desorption measurements, exhibiting first-order desorption kinetics. The adsorbed hydrogen atoms also diffuse into the bulk at 300 K, causing a nearly linear increase in conductivity (∆σ) when the TiO2(110) crystal is exposed to a continuous flow of molecular hydrogen. An initial sticking coefficient of 1 × 10^-6 was reported for H2 adsorption on TiO2(110) at 300 K. In the absence of surface defects, the activation energy to dissociate the H2 molecule is too high, and no adsorption was observed.

A recent study by Pan et al. also reported a very low sticking probability for H2 adsorption on TiO2(110). Low-energy H2+ ion bombardment was employed to enhance the hydrogen adsorption. Surface hydroxyl groups were generated upon hydrogen ion exposures. In addition, the surface Ti3+ coverage was found to increase with increasing hydrogen exposures.

On powdered TiO2 surfaces, Beck et al. reported TPD spectra typical of weakly adsorbed molecular hydrogen. Iwaki observed different adsorption behavior for hydrogen on anatase and on rutile TiO2. On both types of TiO2 powders, chemisorption of hydrogen took place only when hydrogen was introduced above 623 K.

3.2.3. Oxygen Adsorption

Partial charge transfer from the surface adsorption site to the oxygen molecule was found to play an important role for oxygen adsorption on TiO2(110). On the basis of conductivity (∆σ) and surface potential (∆φ) measurements, Göpel et al. proposed the formation of O2- upon chemisorption of oxygen. This step requires the presence of surface defect sites, and is the precursor for further dissociative reactions between the adsorbed O2 and the surface or bulk oxygen vacancies. The initial sticking coefficient is ~8 × 10^-3 at 300 K. The maximum desorption rate for oxygen thermal desorption occurs at ~348 K.

Low-energy ion scattering study by Pan et al. indicated that oxygen adsorption on TiO2(110) occurs at the surface oxygen vacancy sites. With the use of isotope 18O2 adsorption, it was found that no oxygen adsorption would occur on a stoichiometric surface. Kurtz et al. reported that oxygen was dissociated on the surface at 400 K and that the surface Ti3+ sites can be eliminated upon oxygen exposure. Lu et al. found that oxygen molecules adsorb on TiO2(110) at 105 K, and all O2 molecules are dissociated above 400 K.

Beck et al. studied the adsorption of oxygen on powdered rutile TiO2 using thermal desorption measurements. Three different desorption states at 164 K, 416 and ~445 K were identified. Isotope labeling experiments showed no involvement of lattice oxygen in the 164 and 416 K desorption states, and only 7% lattice oxygen was detected in the high temperature peak. For oxygen adsorption on anatase TiO2 powder, only the low temperature state was observed. A recent thermal desorption study by Yanagisawa et al. reported a similar thermal desorption profile for O2 on rutile TiO2. Two desorption features at 180 and 470 K involved only the oxygen from gas adsorption while another desorption state at 520 K included oxygen from both the gas and the lattice.

3.2.4. CO and CO2 Adsorption

Ab initio molecular orbital calculations by Kobayashi et al. showed that CO weakly interacts with a defect-free TiO2(110) surface. The presence of oxygen vacancy defects strongly enhances such interactions due to electron back-donation from surface Ti3+ into the π* orbitals of molecular CO. CO does
not adsorb onto the surface oxygen atoms. Carbonate ion type or colinear carbon dioxide precursor type surface complexes do not exist on the TiO$_2$ surface containing adsorbed CO. At 300 K, Göpel et al.\textsuperscript{75} found that CO adsorbs only at the defect sites. A small amount of CO$_2$ can be formed due to the reaction of adsorbed CO with an adjacent bridging-oxygen atom, resulting in an additional oxygen vacancy. On a single-crystal TiO$_2$(110) surface, Lu et al.\textsuperscript{78} reported a weakly bound CO state desorbing at $\sim$150 K. No thermal dissociation or oxidation was observed.

On a powdered rutile TiO$_2$ surface, Beck et al.\textsuperscript{79} observed two CO desorption states at 175 and 437 K. These states were attributed to CO molecules interacting with the surface oxygen anions through the C-end of CO and CO molecules interacting with the surface defect sites through the O-end of CO, respectively. Infrared spectroscopic studies by Tanaka and White\textsuperscript{82} observed two different molecularly adsorbed CO species with vibrational frequencies at 2185 and 2115 cm$^{-1}$. The lower frequency species was more strongly bound to the surface.

Göpel et al.\textsuperscript{75} also reported that CO$_2$ weakly adsorbed on the TiO$_2$(110) surface and its adsorption was not influenced by the density of surface defect sites. In the presence of surface hydroxyl groups, Tanaka and White\textsuperscript{82} found that CO$_2$ readily reacted to form bicarbonate species on a powdered anatase TiO$_2$ surface.

### 3.2.5. NO and SO$_2$ Adsorption

Lu et al.\textsuperscript{71} studied the adsorption of NO on the TiO$_2$(110) surface and reported a weakly bound molecular adsorption state desorbing at 120 K. In addition, the reduction product, N$_2$O, was observed to desorb at 169 and 250 K. The 169 K desorption feature was observed only on defective surfaces and its intensity was proportional to the surface defect coverage. This low-temperature N$_2$O state was then associated with the NO reductive reaction at surface oxygen vacancy sites, e.g., NO$_{(a)}$ + vacancy $\rightarrow$ N$_{(a)}$ + O$_{\text{lattice}}$, N$_{(a)}$ + NO$_{(a)}$ $\rightarrow$ N$_2$O$_{(a)}$. These defect sites were completely removed upon oxidation by adsorbed NO (to produce N$_2$O).

Similar results were reported by Boccuzzi et al.\textsuperscript{83} for NO adsorption on powdered TiO$_2$ using FT-IR measurements. NO weakly adsorbs on fully oxidized TiO$_2$ at 300 K. On the reduced sample, several molecular and dissociative adsorption states were identified. NO adsorption reoxidized the reduced sample. Thermal desorption measurements by Pande et al.\textsuperscript{84} observed both NO and N$_2$O desorption from NO-exposed TiO$_2$ samples reduced at 523 K. Increasing the reduction temperature (and therefore the defect density) resulted in a higher yield of reduction products (N$_2$O and N$_2$). Only N$_2$O and N$_2$ were desorbed from an NO-exposed sample that was reduced at 1073 K.

Smith et al.\textsuperscript{85} have shown that SO$_2$ also reacts with and oxidizes the oxygen vacancy sites (Ti$^{3+}$) on TiO$_2$-(110) and Ti$_2$O$_3$(1012) surfaces. This reaction continued until all such defect sites were removed by SO$_2$ dissociation. Very weak interaction was observed for SO$_2$ on the nearly perfect TiO$_2$(110) surface. Onishi et al.\textsuperscript{86} investigated the adsorption of SO$_2$ on TiO$_2$(110) and (441) surfaces using X-ray and ultraviolet photoemission spectroscopies (XPS and UPS). On the (441) surface, SO$_2$ oxidized Ti$^{3+}$ to Ti$^{4+}$ accompanied with the formation of S$^{2-}$ species. Only SO$_3^{2-}$ was detected upon SO$_2$ adsorption on the (110) surface at 300 K.

#### 3.2.6. NH$_3$ and H$_2$S Adsorption

Diebold et al.\textsuperscript{87} studied the NH$_3$ adsorption on TiO$_2$-(110) using XPS and low-energy ion scattering (LEIS). A saturation coverage of $\sim$0.16 ML [1 ML = 1 NH$_3$ per surface atom] was measured on the stoichiometric surface. A slightly higher coverage (0.19 ML) was observed on the highly defective surface. Ammonia adsors on TiO$_2$(110) in molecular form. Roman et al.\textsuperscript{88} investigated the same adsorption system using synchrotron radiation UPS. It was found that ammonia weakly adsorbs at 300 K. The uptake was reported to be slightly higher on the perfect surface than on the defective surface. The surface species are predominately molecular ammonia. A small fraction possibly dissociates at the defect sites upon heating the surface to higher temperatures. The saturation coverage is $\sim$0.1 ML at 300 K.

Roman and de Segovia\textsuperscript{89} also investigated the adsorption of ammonia on the TiO$_2$(001) surface using UPS and TPD. Similar to that found on the (110) surface, NH$_3$ molecularly adsorbed on TiO$_2$(001) at 300 K. Molecular NH$_3$ desorbed at $\sim$338 K with first-order kinetics. Some ammonia was dissociated to produce NH$_2$ and OH species. Further decomposition of these products yields desorption of N$_2$ and H$_2$ at 343 and 364 K, respectively.

Smith et al.\textsuperscript{90} studied the interaction of H$_2$S with a highly defective TiO$_2$(110) surface and identified two distinct adsorption states. At low coverages, H$_2$S dissociated to produce H and S atoms bound to surface Ti cation sites. The presence of the adsorbed sulfur atoms dramatically inhibited the oxidation of Ti$^{3+}$ sites by oxygen adsorption. At high H$_2$S exposures, molecular adsorption was observed. This adsorption state can be thermally desorbed before 423 K. Beck et al.\textsuperscript{79} studied the adsorption of H$_2$S on both anatase and rutile powders. Two molecularly adsorbed states (multilayer and monolayer) were observed in thermal desorption spectra on both anatase and rutile. A third irreversible adsorption state was observed only on rutile TiO$_2$ and was attributed to dissociative adsorption at bridge-bonding defect sites.

#### 3.2.7. Deoxygenation Reactions of Organic Molecules on TiO$_2$

On TiO$_2$ surfaces, various coordinatively unsaturated Ti cations (Ti$^{3+}$, Ti$^{2+}$, and Ti$^{4+}$) can be generated by vacuum annealing, Ar$^+$ sputtering, or chemical reductions (using H$_2$ or CO).\textsuperscript{96,69,73,91} It is the relative ease in producing such defect sites that makes the TiO$_2$ surface exhibit not only the acid--base properties of most metal oxides, but also oxidation--reduction reactivities. This is particularly true for the adsorption of oxygen-containing organic molecules which commonly undergo dehydration, dehydrogenation, deoxygenation, and self-disproportionation reactions.
The deoxygenation of alcohols, carboxylic acids, ketones, and aldehydes have been observed on reduced TiO$_2$(100) and TiO$_2$ powder surfaces. Olefins (RCH=CHR) are produced by the reductive coupling of aldehyde (RCHO) molecules at the oxygen vacancy defect sites. Ethylene formation was observed upon formaldehyde adsorption on a defective TiO$_2$(110) surface. The yield of ethylene production was directly correlated to the coverage of surface defect sites. On a reduced TiO$_2$(100) surface, formaldehyde decomposes to adsorbed C, H, and O, which further react upon heating to higher temperatures to produce methoxide species, CO, and CO$_2$. On the fully oxidized (100) surface, formaldehyde undergoes a Cannizzaro-type reaction to simultaneously produce adsorbed methoxide and formate species. The yield of each product is strongly dependent on the preparation procedure of the surface. The formation of dioxymethylene ($\text{-OCH}_2\text{O-}$) has been observed during formaldehyde adsorption on TiO$_2$. Among all the above-mentioned adsorption processes, the deposition or removal of surface oxygen atoms play an essential role.

3.3. Photochemistry of Small Inorganic Molecules on TiO$_2$

3.3.1. Photodecomposition of Water on TiO$_2$

Even though TiO$_2$ can be effectively photoexcited under band-gap irradiation, H$_2$O cannot be photodecomposed on clean TiO$_2$ surfaces. Figure 3.5 illustrates the band-edge positions of TiO$_2$ relative to the electrochemical potentials of the H$_2$/H$_2$O redox couple and the O$_2$/H$_2$O redox couple. According to this electron energy diagram, water photolysis is energetically favorable. However, due to the presence of a large overpotential for the evolution of H$_2$ and O$_2$ on the TiO$_2$ surface, TiO$_2$ alone becomes inactive. Although earlier studies by Schrauzer et al. reported the photosplitting of water using TiO$_2$, Sato and White demonstrated that the hydrogen evolution from wet TiO$_2$ is not due to the photocatalytic splitting of water, but rather the photoassisted oxidation of the oxygen vacancy sites on reduced TiO$_2$. Sustained photodecomposition of water has been achieved under each of the following experimental conditions. Here, each experimental configuration is designed to effectively separate the photogenerated electrons and holes for maximum photo-reaction yield.

(1) A closed circuit photoelectrochemical cell employing a TiO$_2$ anode and a metal (Pt in most cases) cathode, as shown in Figure 3.6. Here, hydrogen evolves from Pt and oxygen from TiO$_2$. A small externally applied electrical potential (>$0.25$ V) may be necessary but this is much smaller than that required in an electrochemical cell for H$_2$O electrolysis (>$1.23$ V). The system was designed to resemble an electrochemical reaction and to effectively separate the photogenerated electrons and holes. The photexcitation of TiO$_2$ injects negatively charged
Photocatalysis on TiO₂ Surfaces

**Figure 3.8.** Photosplitting of water: sacrificial donor effect.

Electrons into the Pt particles and positively charged holes into the RuO₂ particles. Trapped electrons in Pt reduce water to hydrogen and trapped holes in RuO₂ oxidize water to oxygen. The presence of Pt and RuO₂ significantly reduces the overpotential for H₂ and O₂ production, respectively.

(3) The use of sacrificial species to remove one of the photodecomposition products so that the reaction equilibrium is shifted toward further decomposition, as shown in Figure 3.8. Here, the sacrificial species may be oxidized by the hole-reaction product (presumably O₂⁻) or reduced by the electron-reaction product (presumably H₂). For example, when alcohols such as CH₃OH are added to a TiO₂ aqueous suspension, sustained H₂ production is observed upon UV irradiation and the alcohol molecules are oxidized to CO₂. Additional examples about the photooxidation and reduction processes in aqueous TiO₂ systems will be given later in this section.

The detailed mechanism for the photodecomposition of water on TiO₂ and the photooxidation or reduction reactions involving the water–TiO₂ system remains a controversial issue today. A number of researchers have reported the observation of several radical species using EPR measurements. Gonzalez-Elpe et al. reported the formation of HO₂⁻ and O₂⁻ or O₂²⁻ species generated by UV irradiation of hydrated anatase TiO₂ in oxygen. Anpo and co-workers observed OH radicals at 77 K on hydrated anatase under band-gap irradiation. Jaeger and Bard reported the formation of HO₂⁻ and OH radicals in aqueous suspensions of TiO₂. Howe and Grätzel observed that surface hydration of anatase has a significant influence on the reactivity of holes and electrons generated upon band-gap irradiation. Trapped electrons are readily scavenged by adsorbed oxygen. Trapped holes are much less reactive, and they react with surface hydroxyl groups above 77 K to produce O₂⁻. Hydroxyl radicals are not the primary products and their existence is transient.

### 3.3.2. Photoadsorption and Photodesorption of Oxygen on TiO₂

The photoadsorption and photodesorption of O₂ on TiO₂ have been investigated in an effort to understand the electron charge transfer from the substrate to oxygen during adsorption and to understand the electron scavenging process by oxygen during photooxidation of organics. Early investigations of photoadsorption were in fact dealing with the photooxidation of organic contaminants on the TiO₂ surface by the photoactivated oxygen. Courbon et al. suggested the formation of O₂⁻ and O₂²⁻ (O₂ + O²⁻) as the intermediates for photooxidation and photoisotope exchange reactions. Bickley et al. and Munuera et al. studied the photodesorption of oxygen on rutile TiO₂ surfaces and found that the presence of adsorbed water enhances the photodesorption of oxygen by trapping the photogenerated holes at OH⁻ sites. The formation of surface HO₂⁻ by electron trapping (H⁺ + O₂ + 2e⁻ → HO₂⁻) and O₃⁻ by hole trapping reactions (O²⁻(lattice) + O₂ + h⁺ → O₃⁻(lattice)) is the primary route for O₂ photodesorption.

Oxygen photodesorption from powdered TiO₂ was recently studied by Yanagisawa and Ota. It was found that the photodesorption occurs only when photon energy above the TiO₂ band gap was delivered. Oxygen desorbed molecularly, and no isotopic exchange with the lattice was observed. The photodesorption signal followed t⁻¹² decay kinetics, similar to that observed for CO₂ photodesorption from ZnO. These rate kinetics were attributed to the recombination of adsorbed O₂⁻ (or CO₂⁻ on ZnO) with the photogenerated holes.

Lu et al. studied the adsorption of oxygen on a TiO₂(110) surface and similar desorption behavior was observed. No isotopic mixing was detected during the photodesorption experiments even when a mixture of O₁₆O₂ and O₁₈O₂ was adsorbed on the surface.

### 3.3.3. Photooxidation and Photoreduction of Molecular Nitrogen

The photocatalytic activity of TiO₂ for N₂ oxidation and reduction have been observed by several researchers. Schrauzer et al. first reported the photoreduction of N₂ by an iron-doped TiO₂ catalyst. Adsorbed water was photodecomposed to yield oxygen, and at the same time nitrogen was reduced to produce NH₃ and N₂H₄. The hydrogenation of unsaturated hydrocarbons was also achieved photocatalytically in the same study.

Bickley and co-workers studied the photooxidation of N₂ on TiO₂ at the gas–solid interface. Ther-
Photogenerated electrons and holes each get
uct from CO₂ when a Cu-containing TiO₂ suspension
formation of hydroxylated TiO₂ at 300 K. Studies by Hirano et al.¹¹⁴
X-ray photoemission studies. Further oxidation of
since it is a naturally occurring photobiological
12- (or Br⁻, Cl⁻) was detected by several research
Rh, Pt, Au, Cu, or Ru were deposited onto TiO₂
photoreduction selectivity, and reported that meth-
3.3.4. Photoreduction of CO₂
The photoreduction of CO₂ is an important process
since it is a naturally occurring photobiological
process and can be achieved electrochemically. Inoue et al.¹¹³
first reported that a suspension of TiO₂ photocatalyzes the reduction of CO₂ with water to produce formic acid, formaldehyde, methanol, and a
trace amount of methane. Studies by Hirano et al.¹¹⁴
observed methanol as the main photoreduction product from CO₂ when a Cu-containing TiO₂ suspension
was irradiated. Several researchers have designed
experiments to enhance the efficiency and selectivity
for CO₂ photoreduction. The presence of Hg or Pt
seemed to accelerate the formation of formaldehyde or carbon.¹¹⁵ Ishitani and co-workers systematically
investigated the effect of different metals on the
photoreduction selectivity, and reported that meth-
ane and acetic acid are the major products when Pd, Rh, Pt, Au, Cu, or Ru were deposited onto TiO₂
catalysts.¹¹⁶ The Pd–TiO₂ system exhibited very
high selectivity for the production of methane from CO₂
photoreduction. The process can be schematically illustrated in Figure 3.9.

3.3.5. Photooxidation of Halides on TiO₂
Flash photolytic oxidation of halides on TiO₂ were
first conducted on colloidal TiO₂ particles. In the
time-resolved study by Draper and Fox,¹¹⁷ iodide oxidation was monitored on TiO₂ powders and a
direct hole-adsorbate electron transfer process was
suggested. The one-electron oxidation intermediate I⁻ (or Br⁻, Cl⁻) was detected by several research
groups. The formation of I⁻ was studied by Fitz-
amaurice et al.¹¹⁸ by photoirradiation of aqueous I⁻
solution on TiO₂ colloidal particles. It was found that
the photogenerated electrons and holes each get
trapped at surface or subsurface sites. A trapped
hole reacts with an adsorbed I⁻ ion to form an I atom which further reacts with I⁻ to produce I₂⁻:

\[
\begin{align*}
\text{I}^- + \text{h}^+ & \rightarrow \text{I} \\
\text{I}^- + \text{I}^- & \rightarrow \text{I}_2^- \\
2\text{I}_2^- & \rightarrow \text{I}_3^- + \text{I}^- 
\end{align*}
\]

(9)

In the presence of oxygen, electrons are effectively
removed by transferring to adsorbed oxygen. The I₂⁻
will then disproportionate to form I⁰ and I⁻. When
there is no oxygen or other efficient electron scavenger present, trapped electrons will eventually recombine with the holes trapped in I₂⁻ to give back I⁻ ions:

\[
\text{I}_2^- + \text{e}^- \rightarrow 2\text{I}^-
\]

(10)
The photoinduced oxidation of halide on TiO₂
electrodes was also reported.¹¹⁹

3.3.6. Photoinduced Surface Corrosion
Photogenerated electrons and holes diffuse to the
surface region and are trapped at surface or subsur-
face sites where interfacial electron transfer takes
place to induce oxidation and reduction reactions. However, if these trapped charge carriers are not
quickly removed through such reactions, irreversible
chemical changes will occur to the semiconductor
surface layer itself. Studies have shown that both
surface and bulk defects in TiO₂ and ZnO can be
produced upon photoirradiation.¹¹¹ Changes in color
or electrical conductivity are generally good param-
eters for evaluating the extent of photocorrosion. For
example, TiO₂ electrodes in contact with solution
became dark after repeated exposure to UV irradi-
ation.¹²⁰ TiO₂ dissolution occurred under these condi-
tions. However, no such change was observed in the
absence of irradiation. Metal sulfides are especially
easy to corrode upon prolonged photoexposure.¹²¹,¹²²

3.4 Photooxidation on TiO₂ Single Crystals
The photochemical reaction on a TiO₂ catalyst is
generally believed to involve radical species. The
extensive research on photodecomposition of water
and photooxidation of organics has provided some
evidence for such intermediates. However, some
important issues regarding the reactive sites, the
roles of each individual reactant species, and the
detailed mechanisms remain unsettled. Single-
crystal surfaces provide the opportunity to study a
well-ordered structure with known surface area and controlled surface coverages of the reactant molecules
and the surface reactive sites.

3.4.1. Photoelectrochemistry on Single-Crystal Electrodes
Photoelectrochemistry using TiO₂ electrodes was
one of the most active area of research in the 1970s
and early 1980s.¹²³ Most of the research interests
emphasized the photoelectrolysis of water to produce
hydrogen and oxygen. The close connection between
photochemistry and photocatalysis lies in the fact
that both processes involve interfacial electron trans-
ferr (driven by electrical potentials or by photons,
respectively). Most of the fundamental concepts in
photoinduced heterogeneous electron transfer were
either derived from some existing principles of elec-
The interfacial charge transfer (and not the electron-tained in this study suggested that, when the pho-
tooxidation of CHCl₃ by oxygen is conducted in
The electron transfer rate constant cds) ob-
to the degradation of organic pollutants concerns the
size for catalyst particles used in real applications),
Kesselman et al.¹²³ were able to independently evaluate the interfacial electron
portion of the crystal. Feedback control from the thermocouple,
the W-heating leads which are mounted inside the
ative sites for the photodegradation process.

3.4.2. Photochemical Studies on Single-Crystal TiO₂

The only UHV surface science study for the pho-
todegradation of organic pollutants concerns the
molecular oxygen in the water or the TiO₂ lattice was only
ed TiO₂ compared to TiO₂(110) was attributed to
intermediate and was further oxidized into C₀₂. The
oxides and hydroxyl groups participated in the reaction only after the
photooxidation reaction exhibited a threshold energy of ~3.1 eV, the band gap of rutile TiO₂. This study
clearly demonstrated that under UHV conditions
sorbate-mediated photoactivation of adsorbed oxygen
in the key step in the photocatalytic oxidation of
methyl chloride on TiO₂(110). Figure 3.11 schematically
shows the mechanism proposed for this oxidation
process, where O₂⁺ is a generalized symbol for
an activated species whose identity is currently
unknown.

In comparison to the study of photooxidation on
single crystal TiO₂(110), Wong et al.¹²⁴ conducted a
parallel FT-IR study of methyl chloride photooxidation on powdered TiO₂. Consistent results were
obtained which support the conclusions made in the
single-crystal study. Gas phase oxygen must be
present for the reaction to occur, and it was this
oxygen that was incorporated into the oxidation
products. However, the final product from powdered
TiO₂ catalysts was CO₂, not CH₂O. Carbon monox-
ide, which contained exclusively the oxygen from the
gas phase oxygen, was also detected as a reaction
intermediate and was further oxidized into CO₂. The
difference in the photooxidation products on pow-
dered TiO₂ compared to TiO₂(110) was attributed to
the presence of more or different reactive sites on the
powdered TiO₂ which contains both anatase and
rutile (as compared to the single-crystal rutile sur-
face), which allow the oxidation to occur to a larger
extent. It is also possible that the powdered TiO₂
studies involved a greater surface concentration of
O₂(a) due to the higher pressure used compared to
the TiO₂(110) studies in UHV.

Figure 3.10. Design of crystal holder for photochemistry on TiO₂(110) single crystal.

Figure 3.11. Summary of CH₃Cl photooxidation on TiO₂-(110).
3.5. Photooxidation at the Gas–Solid Interface on TiO2 Catalysts

3.5.1 Introduction

In recent years, one of the most active areas of research in photocatalysis concerns environmental decontamination, namely the photomineralization of organic pollutants. TiO2 is used in such studies as the photocatalyst for both gas phase and aqueous suspension systems. The research efforts have aimed at two major photooxidation issues: (1) the identification of reaction intermediates, detailed reaction mechanisms, and reaction kinetics; and (2) the optimization of reaction conditions to enhance the photoreaction rate and yield. The photooxidation in aqueous suspensions will be summarized in section 3.6. Here, a few representative reactions will be discussed for gas phase photooxidation on TiO2 catalysts. Among the gas–solid photooxidation reactions, trichloroethylene (TCE) and chlorophenols (CP) have been most extensively investigated. The oxidation intermediates and the influence of water and oxygen on the overall reaction kinetics have been determined.

3.5.2. The Photoactivity of TiO2: Effects of Adsorbed H2O and O2

Anpo et al. recently studied the influence of water and oxygen on the photocatalytic activity of TiO2. It was found that the adsorption of water on the TiO2 surface caused a decrease in the upward band bending (as shown in Figure 3.12), and therefore an increase in the efficiency for the recombination of photogenerated electrons and holes. This is because in this case the barrier height and width is smaller for the return of a surface trapped electron into the bulk conduction band region. On the other hand, addition of O2 led to an increase in the upward band bending, and therefore suppressed the electron–hole recombination processes leading to more efficient photoactivity. The above conclusions were based on the observed photoluminescence enhancement by H2O adsorption and photoluminescence quenching by O2 adsorption. From a chemical point of view, the adsorbed water then can be regarded as an effective electron–hole recombination center while the adsorbed oxygen can be considered as an effective electron trap to prevent such a recombination process. These results have important implications for gas phase photooxidation processes on TiO2. Some of the observed kinetics can be explained using these concepts.

3.5.3. Trichloroethylene (TCE)

TCE is a common pollutant in air and water due to its wide use as a solvent in industry. The final photooxidation products for TCE on TiO2 are CO2, CO, HCl, and Cl2. For gas phase photooxidation, phosgene (COCl2), dichloroacetyl chloride (DCAC, CHCl2COCl), and sometimes dichloroacetyl acid (CHCl2COOH) in the presence of excess water, have been identified as the oxidation intermediates by several independent research groups.

Phillips and Rauppi studied the reaction kinetics and found that in the absence of water vapor, the TiO2 catalyst exhibited a high initial photoactivity which then declined rapidly with time. At low water vapor pressure, the photooxidation rate is independent of the water partial pressure, whereas at higher partial pressure the reaction rate is strongly inhibited by the water vapor. Oxygen showed second-order kinetics which shifted to zeroth order with increasing oxygen pressure. On the basis of the kinetics data, the authors suggested that the photoproduction of hydroxyl radical (•OH) and hydroperoxide radicals (HO2•, O2•−) was the rate-determining step. However, it was not determined which radical species attacked the TCE molecule and induced the photooxidation.

Fan et al. studied this reaction using isotopically labeled oxygen and water. Similar reaction intermediates and products were identified (that is, DCAC, phosgene, CO, CO2 and surface carboxylate groups). Figure 3.13 shows the isotope induced vibrational frequency shifts in these compounds in the gas phase when TCE is oxidized by oxygen (18O2 or 16O2) on hydroxylated TiO2. It is quite obvious that only oxygen atoms from the gas phase oxygen are incorporated into the intermediates (DCAC, phosgene, CO), while isotope mixing occurs in CO2. This is probably due to the formation of carboxylates on the surface (which involve lattice 16O as an intermediate for the release of final product, CO2). Therefore, the initial oxidation of TCE involved exclusively the gas phase O2-derived active radical species (HO2•, O2•−, etc.) and not the hydroxyl radicals from direct hole trapping by surface hydroxyl groups.

Larson and Falconer analyzed the surface composition of the TiO2 catalysts during and after TCE photooxidation reactions. Their results implied that the accumulation of Cl ions and other reaction intermediates may poison the TiO2 catalyst for
further TCE photooxidation; the presence of water (either vapor or liquid) helped to remove these surface species.

3.5.4. 4-Chlorophenol (4-CP)

Photodegradation of 4-chlorophenol has been investigated in gas phase, in aqueous suspension, and on electrodes. The molecule is of interest due to its benzene ring structure which allows the capture of radical intermediates (such as \(' OH\)) or the direct interaction with an electron. A recent FT-IR study of the gas phase reaction by Stafford et al. found that in the absence of water vapor, 4-CP was photooxidized possibly by reacting with the photogenerated \(' O_2^-\) radical species. Addition of water vapor to the system dramatically enhanced the rate and extent of photooxidation. However, the exact cause for this change was not determined. Direct reaction of 4-CP with photogenerated electrons was also observed. 4-CP accepts one electron and releases one Cl\(^-\) ion, resulting in hydroquinone formation. Futher photooxidation required the presence of oxygen. From these results, the authors pointed out that hydroxyl radicals ('OH) may not be exclusively responsible for the photooxidation of 4-CP and the role of oxygen is more than that of merely an electron scavenger.

3.6. Photooxidation at the Liquid–Solid Interface on TiO\(_2\) Catalysts

3.6.1. Introduction

By using TiO\(_2\) as a catalyst, the photooxidation of organics may be used for decontamination treatment in polluted waters. Such applications have inspired a vast amount of research. The solid photocatalysts studied include colloidal particles, high surface area powders, and single-crystal surfaces. The complexity of the liquid–solid interface presents many more variables (in comparison to the gas–solid system) to be dealt with in kinetics studies. Such parameters include the surface composition, surface area, preparation procedures, and concentration of the photocatalyst; the pH of the solution and its effect on the surface structure; the concentration of the reactants; the solvent environment; the partial pressure of oxygen; the diffusion rate in solution and near the surface, etc. Care must be taken with the controllable parameters, or discrepancies will occur in the experimental results. For instance, chlorobenzene was first reported not to undergo complete mineralization over TiO\(_2\). However, experiments with a differently prepared TiO\(_2\) catalyst and with a higher oxygen pressure demonstrated that total photooxidation of chlorobenzene may be achieved. The various kinetic parameters in the liquid–solid photooxidation systems have been discussed in several recent reviews.

3.6.2. The Primary Events of Photooxidation at the Liquid–Solid Interface

Continuous band-gap irradiation of an aqueous semiconductor dispersion excites an electron from the valence band to the conduction band, creating an electron–hole pair. The electrons possess the reduc-
ns in a semiconductor particle, and the hole trapping can compete with the recombination process. In the trapped state, holes are relatively unreactive toward electrons. At a high concentration of electron–hole pairs, the charge carriers recombine within a fraction of one nanosecond. Therefore, the interfacial carrier trapping must be very rapid in order to achieve effective photochemical conversion. This requires the electron or hole trapping species to be preadsorbed on the catalyst surface.

Gerischer and co-workers recently analyzed the photooxidation kinetics of organic molecules on TiO₂ particles in aqueous environment. It was found that the rate of photooxidation is equal to and limited by the reduction rate of dissolved oxygen (O₂) in the solution. It was theoretically predicted and experimentally confirmed that when O₂ is not reduced at a sufficiently high rate, electrons accumulate on the photocatalyst particles, and the rate of radiationless recombination is enhanced until the sum of the electron–hole recombination and the electron transfer to O₂ is equal to the rate of the hole photogeneration. The deposition of Pd metal particles on TiO₂ enhances the electron transfer to O₂ and eliminates the electron accumulation on the TiO₂ particles.

3.6.4. Overview of Photomineralization Reactions in Aqueous Semiconductor Dispersions

In an aqueous TiO₂ suspension, the holes in the TiO₂ valence band have enough oxidizing power to convert any organic species to CO₂, water, and mineral acids (such as HCl). The photogenerated holes in the semiconductor particles, the hole-trapping radical species, and the activated oxygen species (by electron trapping) are all strong oxidation agents for organic compounds. The nonselective and total photooxidation property of the system has been applied for water purification by the photomineralization of organic pollutants. Almost every major class of organic contaminant has been examined for possible degradation using this technique. Detailed mechanistic analysis of these reactions have appeared in several recent reviews and shall not be repeated here.

4. Surface Modifications

4.1. Introduction

As was stated earlier in this review, one of the most active fields of research in heterogeneous photocatalysis using semiconductor particles is the development of a system capable of using natural sunlight to degrade a large number of organic and inorganic contaminants in wastewater. The overall photocatalytic activity of a particular semiconductor system for the stated purpose is measured by several factors including the stability of the semiconductor under illumination, the efficiency of the photocatalytic process, the selectivity of the products, and the wavelength range response. For example, small band-gap semiconductors such as CdS are capable of receiving excitation in the visible region of the solar spectrum, but are usually unstable and photodegrade with time. On the other hand, TiO₂ is a quite stable photocatalyst, but since the band gap is large (E_g = 3.2 eV) it is only active in the ultraviolet region which is <10% of the overall solar intensity as shown in Figure 4.1.

The limitations of a particular semiconductor as a photocatalyst for a particular use can be surmounted by modifying the surface of the semiconductor. To date, three benefits of modifications to photocatalytic semiconductor systems have been studied: (1) inhibiting recombination by increasing the charge separation and therefore the efficiency of the photocatalytic process; (2) increasing the wavelength response range (i.e., excitation of wide band gap semiconductors by visible light); and (3) changing the selectivity or yield of a particular product. A few examples will be given in the following sections illustrating the large body of work conducted in the area of photocatalyst surface modification.

4.2. Metal Semiconductor Modification

In photocatalysis the addition of noble metals to a semiconductor can change the photocatalytic process by changing the semiconductor surface properties. The metal can enhance the yield of a particular product or the rate of the photocatalytic reaction. The enhancement in reactivity was first observed for the photoconversion of H₂O to H₂ and O₂ using the Pt/TiO₂ system. The addition of a metal to a semiconductor surface can also change the reaction products.

Figure 4.2 is an illustration of the electron capture properties at the Schottky barrier of the metal in contact with a semiconductor surface. The picture schematically illustrates the small area of the semiconductor surface that the metal actually covers. Transmission electron microscopy measurements have found that when the added metal is Pt, the Pt particles form clusters on the surface. With a Pt dose of 10 wt %, only 6% of the semiconductor surface area is covered. Therefore a large surface area of the semiconductor is still exposed.

After excitation the electron migrates to the metal where it becomes trapped and electron–hole recombination is suppressed. The migration of electrons to the metal particles was confirmed by studies showing the reduction in the photoconductance of the semiconductor particle.

Figure 4.1. Solar spectrum at sea level with the sun at zenith.
photocatalysis on TiO$_2$ surfaces  

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Figure 4.2. Metal-modified semiconductor photocatalyst particle.

Figure 4.3. Photocatalysis in composite semiconductor—semiconductor photocatalyst.

The Pt-modified TiO$_2$ compared to TiO$_2$ alone$^{148a}$ The hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur.

The Pt/TiO$_2$ system is the metal-semiconductor system most commonly studied. As was previously stated, the photostability of TiO$_2$ and the capability of band-gap excitation in the solar region make it the semiconductor of choice. The addition of Pt to the TiO$_2$ surface is beneficial for photocatalytic reactions evolving gas, especially hydrogen. The metal is important also because of its own catalytic activity. The metal actually modifies the photocatalytic properties of the semiconductor by changing the distribution of electrons. The effect of added metal to the semiconductor's electronic properties was explained in section 2.2.5. When the two species come in contact the Fermi levels of the metal and semiconductor align causing electrons to flow to the metal from the semiconductor. The decrease in electron density within the semiconductor leads to an increase in the hydroxyl group acidity$^{148b}$. This in turn affects the photocatalytic process on the semiconductor surface.

The electronic modification of the semiconductor surface via metal deposition can also be observed with other noble metals. The addition of silver to the TiO$_2$ surface does increase the production of H$_2$ from alcohol. The increase in H$_2$ production is attributed to the trapping of electrons at the metal sites. The increase in H$_2$ production for the Ag/TiO$_2$ photocatalyst is not as great as the increase in H$_2$ production for Pt/TiO$_2$.$^{149}$

TEM has determined that the size of Pt particles remained the same over the 0.5–10% Pt range of content on the TiO$_2$ surface. The Pt particles have a mean diameter of 2 nm.$^{147}$ There is an optimum loading of Pt (1.0 wt %) to achieve a maximum photocatalytic rate of hydrogen production from alcohols. This shows that the morphology or geometrical factor does not affect the photocatalytic properties of the mixed system but an optimum Pt content affects the distribution of electrons in the system. Above the optimum metal content the efficiency of the photocatalytic process actually decreases. Care must be taken when studies are conducted on a metal-modified semiconductor to work with the quantity of metal which gives the optimum photocatalytic efficiency.

4.3. Composite Semiconductors

Coupled semiconductor photocatalysts provide an interesting way to increase the efficiency of a photocatalytic process by increasing the charge separation, and extending the energy range of photoexcitation for the system. Figure 4.3 illustrates geometrically and energetically the photoexcitation process for the composite (coupled) semiconductor—semiconductor photocatalyst CdS—TiO$_2$. Transmission electron micrographs of the coupled semiconductors shows the direct geometrical interaction of multiple CdS particles with the TiO$_2$ particle surface.$^{149}$ The relative positions of the conduction and valence band energy levels for the two semiconductors are referenced to the vacuum level (see Figure 2.4). The energy of the excitation light is too small to directly excite the TiO$_2$ portion of the photocatalyst, but it is large enough to excite an electron from the valance band across the band gap of CdS ($E_g = 2.5$ eV) to the conduction band. According to this energetic model in Figure 4.3, the hole produced in the CdS valence band from the excitation process remains in the CdS particle while the electron transfers to the conduction band of the TiO$_2$ particle. The electron transfer from CdS to TiO$_2$ increases the charge separation and efficiency of the photocatalytic process. The separated electron and hole are then free to undergo electron transfer with adsorbates on the surface. The quantum yield for the reduction of methylviologen drastically increased and approached an optimum value of 1 when the concentration of TiO$_2$ was increased in a CdS—TiO$_2$ system.$^{150}$

Transient absorption spectra of the composite CdS—TiO$_2$ photocatalyst indicate trapping of the electron at Ti$^{4+}$ sites on the TiO$_2$ surface. The CdS—TiO$_2$ system exhibits a broad absorption band in the 550–750 nm region after receiving a 355 nm (3.5 eV)
Figure 4.4. Excitation steps using dye molecule sensitizer.

picosecond laser pulse. This band is characteristic of chemical changes associated with the trapping of electrons on the TiO₂ surface. The lack of absorption activity in the 550–750 nm region was tested by using the same laser pulse with the TiO₂ particles alone. Only the CdS portion of the composite photocatalyst exhibited an absorption band in the visible region. The transient absorption spectrum showed no absorption on clean TiO₂. The experimental results show that the coupling of semiconductors with the appropriate energy levels can produce a more efficient photocatalyst via better charge separation.

4.4. Surface Sensitization

Surface sensitization of a wide band-gap semiconductor photocatalyst (TiO₂) via chemisorbed or physisorbed dyes can increase the efficiency of the excitation process. The photosensitization process can also expand the wavelength range of excitation for the photocatalyst through excitation of the sensitizer followed by charge transfer to the semiconductor.

Some common dyes which are used as sensitizers include erythrosin B, thiourea, and analogs of Ru(bpy)₃²⁺. Figure 4.4 illustrates the excitation and charge injection steps involved for the regenerative dye sensitizer surface process. Excitation of an electron in the dye molecule occurs to either the singlet or triplet excited state of the molecule (see Figure 2.2). If the oxidative energy level of the excited state of the dye molecule with respect to the conduction band energy level of the semiconductor is favorable (i.e., more negative), then the dye molecule can transfer the electron to the conduction band of the semiconductor. The surface acts as a quencher accepting an electron from the excited dye molecule. The electron in turn can be transferred to reduce an organic acceptor molecule adsorbed on the surface. A study has been conducted which demonstrates the reduction of N,N,N’,N’-tetraethyloxonine by a sensitized TiO₂ system. The sensitizer was anthracene-9-carboxylic acid which extended the response of TiO₂ into the visible region, λ = 450 nm. In this system a redox couple was employed to regenerate the dye sensitizer. Without the presence of a redox couple, the dye sensitizer semiconductor system can also be used in oxidative degradation of the dye sensitizer molecule itself after charge transfer. This is important due to the large quantity of dye substances in wastewater from the textile industries.

4.5. Transition Metal Doping

The influence of dissolved transition metal impurity ions on the photocatalytic properties of TiO₂ has become another interesting area of semiconductor modification. The benefit of transition metal doping species is the improved trapping of electrons to inhibit electron–hole recombination during illumination. With Fe³⁺ doping of TiO₂, an increase in Ti³⁺ intensity was observed by ESR upon photoirradiation due to trapped electrons. Only certain transition metals such as Fe³⁺ and Cu²⁺ actually inhibit electron–hole recombination. The concentration of the beneficial transition metal dopants is very small and large concentrations are detrimental. Other transition metal dopants such as Cr³⁺ create sites which increase electron–hole recombination. It is believed that these transition metals create acceptor and donor centers where direct recombination occurs. Compared to the other areas of surface modification, the amount of work conducted on the photoreaction of different organic species with transition metal doped TiO₂ systems is very small.

5. Summary

In a heterogeneous photocatalysis system, the efficiency for chemical transformation depends on the photoactivity of the adsorbate molecules and the catalyst substrates. In the case of an inert oxide substrate, electron transfer or energy transfer events occur between the adsorbate molecules. The catalyst only provides an ordered environment for a more efficient molecular interaction and does not participate in the photoexcitation or chemical reaction process. The chemical reactions induced by photon absorption and the subsequent relaxation is determined by the nature of the adsorbate molecular structure.

In the case of a reactive semiconductor substrate, the catalyst can either provide energy levels to mediate electron transfer between adsorbate molecules (by temporarily accommodating an electron) or behave as both an electron donor (the photogenerated electron in the conduction band) and an electron acceptor (the photogenerated hole in the valence band). Here, the band structure of the substrate plays a significant role. A change in the surface and bulk electronic structure can dramatically alter the chemical events following photoexcitation of the adsorbate molecules or the catalyst substrate.

Applications of heterogeneous photocatalysis to environmental cleanup involve the use of photocatalysts for the non-selective total oxidation of organic pollutants. TiO₂ is photoactive in the UV region (<400 nm) and is currently considered the most promising catalyst for air and water photocatalytic
decontamination. Water and oxygen molecules are considered necessary for the photooxidation process, however, very different kinetics effects by these two surface species have been reported by different authors and for different compounds. For gas–solid systems, it has been shown that molecular oxygen is necessary for the photooxidation to occur while water is necessary to remove from the catalyst surface some of the reaction intermediates or products, the accumulation of which may poison the catalyst. For aqueous TiO₂ suspensions, it is believed that the ‘OH radicals from hole-trapping by surface hydroxyl groups are the primary oxidizing agents and oxygen is a scavenger for photogenerated electrons. However, for aqueous TiO₂ suspensions, there is currently no isotope labeling experiment to definitively show which species (H₂O or O₂) is more transfer can be dramatically influenced. The application of photochemical transformation methods is a rich area for both basic scientific research and technological development.

6. Acknowledgments

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7. References

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