FUNDAMENTALS AND PRINCIPLES OF PHOTOCATALYSIS

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Keywords

Semiconductor photocatalysts, Band gap engineering, Electron–hole recombination, Reactive oxygen species, Charge carrier dynamics, Heterogeneous photocatalysis

Received - *16th December 2025*

Online Available - *13th January 2026*

Abstract

Photocatalysis provides a renewable platform to address both environmental and energy problems by converging air cleaning or less harmful products. This chapter overviews the principles of gas-phase photocatalysis, highlighting mechanistic similarities and differences between oxidative pollutant degradation and reductive pollutant conversion. Photocatalytic oxidation of major pollutants including volatile organic compounds (VOCs), nitrogen oxides (NOX), and sulfur oxides (SOX). The reductive reactions provide transferable insights for carbon dioxide (CO2) reductions. CO2 photoreduction is highlighted, with discussion devoted to mechanistic insight, material design pathways including defect engineering, doping, heterojunction engineering, cocatalyst loading and organic interlayers, and control of selectivity and product proof standards. Case studies are included to show recent progress in increasing efficiency and stability. This chapter concludes by providing a critical account of current limitations and suggesting potential futures for developing scalable photocatalytic systems capable of sustaining simultaneously both clean technologies for air and sustainable CO2 utilization.

1. Introduction

Photocatalysis is a rapidly developing area of study; using photon-excited electrons in a catalyst to drive chemical reactions (which are thermodynamic) Photocatalysis was developed from a fundamental interest in 1972 when Fujishima and Honda first demonstrated photoelectrochemical water splitting using a TiO_2 electrode [1]; since then, the field has expanded to address global issues in both energy security and environmental sustainability [2].

In current research, photocatalysis is viewed as an interaction between semiconductor physics, surface chemistry and reaction engineering. Advancements in nano-technology, defect-engineering and computational modeling have significantly improved the understanding of the mechanisms behind photocatalytic processes [3]. While significant advancements have been made, photocatalysts still suffer from a number of intrinsic limitations including rapid recombination of charge carriers, limited spectral range and poor reaction specificity [4].

This Chapter will provide a review of the fundamental principles of photocatalysis with an emphasis on the electronic structure of photocatalysts, charge dynamics and reaction mechanisms. The discussions in this Chapter will be organized in a way to illustrate the important design considerations involved in the development of modern photocatalysts; thus, this Chapter provides a general foundation for the special topics of this book that are discussed in subsequent chapters.

2. Photocatalytic Fundamentals

A semiconductor absorbs light in order to catalyze a reaction. The mechanism is initiated when an electron (e-) is transferred to the conduction band (CB) from the valence band (VB) of the semiconductor upon absorbing photons that have at least the amount of energy required to overcome the band gap of the semiconductor. As the electron is elevated to the conduction band, it generates a positive hole (h+) in the valence band [5,6]. The generated charge carriers move to the catalyst surface where they can be used

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Godse (2026) Advances in Photocatalysis: Principles, Materials and Applications, https://doi.org/10.5281/zenodo.18229789

in oxidation/reduction reactions with adsorbed species.

Photocatalysts may be categorized into two main classes of photocatalysts; homogeneous and heterogeneous. Homogenous photocatalysts contain both the catalyst and reactants in the same phase, usually in solution, while heterogeneous photocatalysts consist of a solid semiconductor catalyst in contact with liquid or gas phase reactants. While there has been extensive research on both types of photocatalysts, heterogeneous photocatalysts offer more stable, recyclable and applicable properties in addition to other benefits [7].

In order to be considered an effective photocatalyst, the photocatalyst should meet five important requirements [8,9]; (i) strong optical absorption over a wide spectrum, (ii) correct positioning of the band edges to thermodynamically drive the desired redox reaction, (iii) efficient transfer of photogenerated charge carriers to the catalyst surface, (iv) large surface area and high density of reactive sites to facilitate reactant adsorption and (v) high degree of chemical and photochemical stability during operation. The relative importance of each of the above factors will determine the photocatalytic activity of the system as illustrated by the basic photocatalytic process shown schematically in Fig. 1.

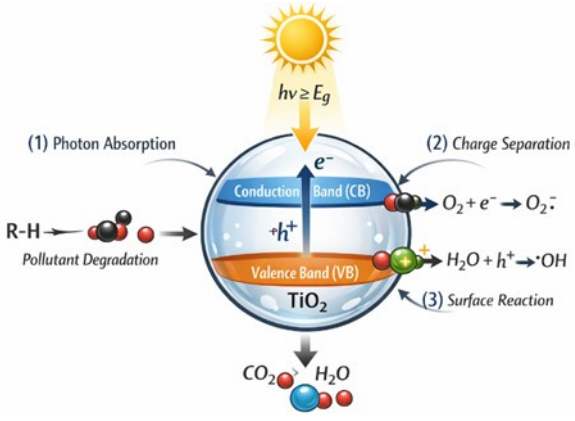

Fig. 1: Electronic Structure and Band Gap of Semiconductors

3. Electronic Structure and Band Gap of Semiconductors

The electronic structure of a semiconductor is the foundation for the semiconductor's ability to act as a photocatalyst. The energy difference between the top of the valence band (VB) and bottom of the conduction band (CB) is termed the bandgap. The bandgap defines the wavelength of light that the semiconductor will absorb [10]. Materials with large band gaps (TiO_2 ~3.2 eV), tend to absorb mostly UV radiation; however, materials with smaller band gaps or engineered materials are able to absorb visible radiation, which accounts for a greater proportion of the solar spectrum [11].

Additionally, the position of each band edge determines the thermodynamic feasibility of chemical reactions at the surface of the semiconductor. The CB must be more negative than the reduction potential of the desired product (e.g., H^+/H_2, CO_2/CH_4), while the VB must be more positive than the oxidation potential (e.g., H_2O/O_2, $OH^-/•OH$) [12]. The band structure can be manipulated using methods such as elemental doping, creating a solid solution, introducing defects into the crystal lattice and forming heterostructures—collectively referred to as bandgap engineering [13,14]—to meet this thermodynamic requirement. A representation of the required relationship between the bands is shown in the typical band energy diagram (Figure 2).

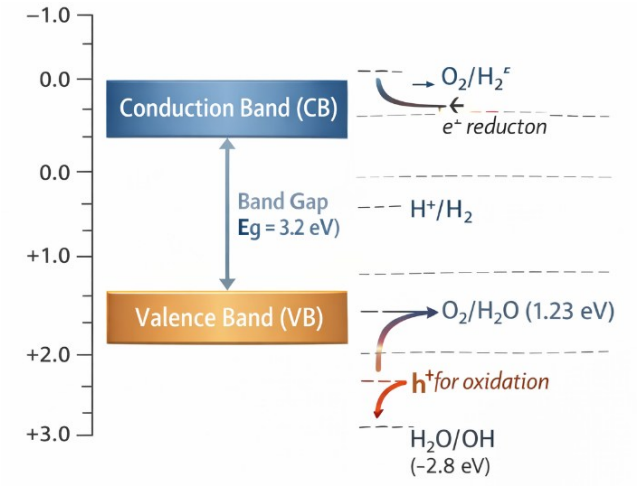

Fig. 2: Typical band energy diagram

Following the photo-generation of electron-hole pairs, competing mechanisms of charge separation and recombination ensue. The recombination process, where the absorbed energy is released as heat, or light, is a significant loss mechanism limiting the quantum efficiency of photocatalysis [15]. This loss mechanism can be either volume recombination within the bulk of the semiconductor material or surface recombination on the semiconductor's surface. Factors affecting the rate of recombination

are primarily influenced by factors including; the semiconductor material's crystallinity, its particle size, the density and type of defect states present within the material. The benefits of nanostructuring to limit volume recombination through reduction of the diffusion distance from the interior to the surface of the semiconductor have been demonstrated [16]. However, excessive surface defects can serve as recombination sites and thus offset the benefit [17].

As Kamat [20] has stated, an essential component of creating efficient photocatalyst systems is to effectively manipulate charge transfer across interfacial boundaries to maximize charge carrier lifetime and overall photocatalytic activity. Researchers have employed various techniques to minimize recombination losses, including cocatalyst loading (i.e., Pt, CoOx), heterostructure formation (i.e., type II, Z-scheme), surface passivation and incorporation of conductive supports such as reduced graphene oxide [18,19].

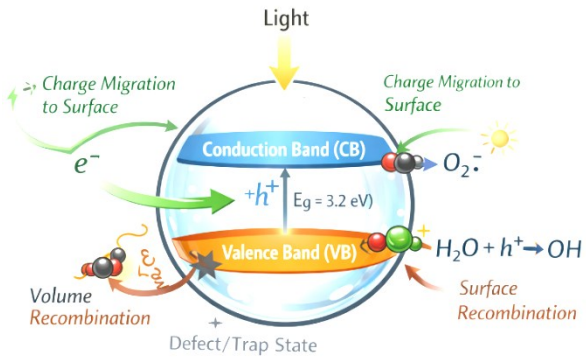

Fig. 3: Charge Carrier Dynamics and Recombination Pathways

4. Mechanism of Photocatalysis

The mechanism for photocatalysis is a multi-step process that begins upon the generation and subsequent migration of the charge carriers generated at the semiconductor-liquid interface. Once formed and migrated to the surface, the charge carriers undergo redox chemistry to either remove the pollutant from the surface through oxidation/reduction reactions [21].

Valence band holes are strong oxidizing agents that can directly oxidize surface adsorbed contaminants or surface bound hydroxide (-OH) and/or water (H_2O) to produce the highly reactive oxygen species (ROS): hydroxyl radicals (•OH) [22]. At the same time, conduction band electrons can also reduce adsorbed oxygen (O_2) to form the ROS: superoxide radical anion ($O_2^{\bullet-}$) which can be transformed into other ROS: H_2O_2 and •OH [23].

In addition to their role in creating the necessary environment for pollutant degradation, holes are used to drive the oxygen evolution reaction (OER) ($4h^+ + 2H_2O \rightarrow 2H^+ + O_2$) in energy applications including water-splitting; whereas electrons will drive the hydrogen evolution reaction (HER): ($2e^- + 2H^+ \rightarrow H_2$) [24].

In addition, electrons will also mediate multi-electron transfers in the reduction of CO_2 to produce products such as CO, CH_4 and CH_3OH [25].

Although there is a well understood framework for photocatalysis, the slow kinetics and unwanted secondary reactions continue to be major barriers to more efficient and selective photocatalytic systems.

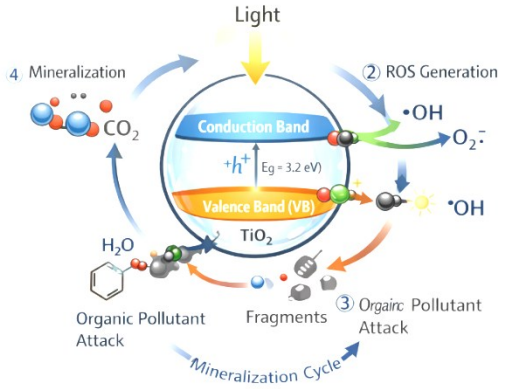

Fig. 4: Integrated Mechanism for Photocatalytic Pollutants Degradation

5. Summary

In this Chapter the main aspects of Photocatalysis are presented including; Light Absorption, Electronic Structure, Charge Carrier Dynamics and Surface Reaction Mechanisms. Understanding these key factors is necessary to develop high performance photocatalysts through rational design. All the aspects covered here (band alignment to recombination suppression) provide a fundamental scientific basis for the development of new materials and application ideas, which will be described in detail in the next Chapters.

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