A COMPREHENSIVE REVIEW OF PHOTOCATALYTIC MATERIALS: FROM FUNDAMENTALS TO EMERGING FRONTIERS

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Abstract

Photocatalysis is an environmentally friendly, sunlight-powered method of addressing two global crises: the crisis of energy scarcity and the environmental pollution crisis. In this chapter we have reviewed all photocatalytic material developments from the first reported use of titanium dioxide (TiO2) to current multi- component photocatalysts. The basic photochemistry of photocatalytic reactions are described in detail by explaining how light is absorbed by the photocatalyst, how electrons move through the semiconductor, and where chemical changes occur at the surface of the photocatalyst. We have also analyzed the limitations of traditional semiconductors (TiO2 and ZnO) based on their inability to activate photons using wavelengths corresponding to visible light and their tendency to undergo photocorrosion. We have also explored the engineering of photocatalytic materials including the modification of band gaps using dopants made of metals and nonmetals, and the addition of graphene or carbon nanotubes (CNTS). Additionally, we have explored the use of plasmon and magnetically active photocatalysts. The chapter also discusses the transition from the use of single-component photocatalysts to the use of more complex heterojunction structures (Type-II, Z-scheme, and S-scheme) that provide improved charge separation efficiency while providing high redox potential. The chapter concludes by highlighting new photocatalytic materials that have been developed recently such as g-C3N4, MOFs, and perovskites. The synthesis of these materials and the future of scaling up the production of these materials for industry are discussed in the final section of the chapter.

1. Introduction

Photocatalysis is an area of study that has garnered interest due to the global issues of energy sustainability and environmental remediation. It is often referred to as "artificial photosynthesis" because it uses sunlight to convert energy into chemical energy. In 1972, Fujishima and Honda were the first scientists to demonstrate the feasibility of using solar light to split water at a TiO_2 electrode [1]. Since then, Photocatalysis has evolved to be a multidisciplinary field of study encompassing materials science, surface chemistry, nanotechnology, and environmental engineering.

The primary advantage of Photocatalysis is that it can use solar radiation to induce chemical reactions at ambient conditions without additional energy input. Unlike the conventional thermal or chemical methods used in industry, the chemical reactions involved in photocatalysis occur at room temperature and under atmospheric pressure and therefore generate minimal amounts of harmful byproducts. These advantages make photocatalysis very attractive from a green chemistry perspective, particularly for wastewater treatment, air cleaning, hydrogen production, and CO2 conversion [2].

However, despite its conceptual simplicity, there are several material-related challenges associated with the implementation of photocatalysts, such as low visible light absorption, rapid recombination of photoinduced charge carriers, slow reaction rates between reactants and catalyst surfaces, and difficulty in recycling of the catalyst. As a result, researchers

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have focused their efforts toward developing new photocatalytic materials to address these material-related challenges. This chapter will review the history of photocatalytic materials, starting with traditional metal oxide photocatalysts and ending with complex heterojunctions, carbon-based composites, ferrite magnetophotocatalysts, and newly evolving hybrid photocatalysts.

2. Thermodynamics and Kinetics of Photocatalysis

Understanding photocatalytic materials requires an understanding of the thermodynamic and kinetic processes that govern the chemical reactions induced by light. Photocatalysis involves multiple steps in the photoconversion of chemicals into other products, including photon absorption, charge carrier formation, charge carrier migration, surface reaction, and finally charge carrier recombination.

2.1 Photon Absorption and Formation of Excitons

Photocatalysis commences when a semiconductor absorbs photons with energies equivalent to or greater than the bandgap energy (Eg) of the semiconductor. The absorption of the photon causes the promotion of an electron from the valence band (VB) to the conduction band (CB), forming an electron-hole pair (exciton). The positions of the CB and VB edge levels relative to the standard redox potentials determine the oxidative/reductive capabilities of the photocatalyst.

In order for photocatalysis to be efficient, the CB edge level of the photocatalyst must be reduced to a level sufficient to allow for reduction reactions to occur (e.g. O2 → •O2− or H+ → H2). On the other hand, the VB edge level must be elevated sufficiently to allow for oxidation reactions to occur (e.g. H2O → •OH). Therefore, the restriction on available semiconductor materials is significant due to this energetic requirement [3].

2.2 Migration and Recombination of Charge Carriers

After the formation of the electron-hole pair, the charge carriers must migrate from the interior of the photocatalyst to the surface before they undergo recombination. However, recombination occurs rapidly on femtosecond to nanosecond time scales and results in a loss of photocatalytic efficiency. In fact, studies have shown that in some cases over 90% of the photogenerated charge carriers undergo recombination prior to participating in a surface redox reaction [4]. Strategies for suppressing recombination include doping, hetero-junction formation, surface modification, and nanostructuring, all of which create internal electric fields, trap states, or direct paths for charge carrier transport.

2.3 Surface Oxidation/Reduction Reaction

Upon reaching the surface of the photocatalyst, the electrons and holes participate in oxidation/reduction reactions with adsorbed species. The holes cause the oxidation of water or hydroxide ions to produce highly reactive hydroxyl radicals (•OH), whereas the electrons cause the reduction of molecular oxygen to produce superoxide radicals (•O2−). These reactive oxygen species (ROS) are the primary agents responsible for the destruction of organic pollutants and the inactivation of microorganisms.

3. Traditional Metal Oxide Semiconductors

3.1 Anatase Titanium Dioxide Photocatalysis

Titanium dioxide (TiO(2)) continues to be the most extensively researched photocatalysts for their chemical stability, nontoxicity, and natural availability along with their ability to generate powerful oxidants. Anatase TiO(2), rutile TiO(2), and brookite are the three main crystalline structures of titanium dioxide.

The primary reason that anatase TiO(2), with a bandgap of approximately 3.2eV, exhibits better photocatalytic performance is because it possesses a greater surface area compared to rutile TiO(2) and a lower recombination rate of charge carriers and therefore better charge transport properties. Rutile TiO(2), which is thermodynamically more stable and also possesses a slightly smaller bandgap (approximately 3.0eV), usually does not exhibit the same level of photocatalytic activity when used individually.[5]

Degussa P25 is a type of mixed-phase TiO(2) system consisting of approximately 80% anatase and 20% rutile. Degussa P25 demonstrates enhanced photocatalytic performance relative to both pure anatase and rutile TiO(2). This is due to the synergistic charge carrier transfer between the anatase-rutile phase interfaces of Degussa P25, thereby creating an intrinsic heterojunction which inhibits recombination.

3.2 Zinc Oxide and Photostability Issues

Zinc oxide (ZnO) is a wide bandgap semiconductor material (approximately 3.2eV) which has a number of attractive physical properties including high electron mobility, a large exciton binding energy (approximately 60meV), and a high absorption coefficient for UV light. As a result, zinc oxide has been used in a variety of applications including photocatalytic oxidation of organic contaminants, antibacterial agents, and photoelectrochemical applications. Furthermore, in some studies, zinc oxide has demonstrated higher quantum efficiencies than titanium dioxide due to the superior charge transport properties of zinc oxide and the richer surface defect chemistry of zinc oxide.

However, despite these advantageous properties, zinc oxide is highly susceptible to photocorrosion in aqueous environments, especially in environments where the pH is low and/or there is limited oxygen. The fundamental reason for this instability is the ease with which Zn-O bonds can be broken by either oxidative or reductive dissolution processes. When illuminated, photogenerated holes in the valence band of ZnO can oxidize the lattice ZnO through the following reaction:

$$ZnO+2H+\rightarrow Zn2++1/2O2$$

The loss of Zn^{2+} ions is permanent, the catalyst is structurally damaged and the catalysis activity decreases gradually. Simultaneously, due to the very strong reductive conditions, the conduction band electrons can reduce the surface oxygen species, which causes the crystal lattice to be de-stabilized.

ZnO has therefore a low durability in the course of prolonged photocatalytic cycles and is hence limited for long term use in practice.

A number of parameters influence the photocorrosion; pH, the amount of dissolved oxygen and the surface defect density. The acidic environment accelerates the dissolving of Zn^{2+}, whereas in an alkaline environment the ZnO is stabilized on the surface by hydroxyl groups. However, in case of too much hydroxilation, it can inhibit the active sites and the photocatalytic performance.

Furthermore, the oxygen vacancy, which contributes positively to the charge separation, can contribute negatively as well, if there is a high concentration of them, as they can be initiation sites for the lattice breakdown.

Therefore, numerous methods for modifying materials have been developed in order to overcome the above mentioned restrictions. By doping ZnO with metals or nonmetals (e.g., Al, Ga, N, S) the electronic structure of ZnO can be altered in a way that suppresses the self-oxidation and reduces the accumulation of holes at the surface.

Surface passivation of ZnO using inert oxide shells (SiO_2, Al_2O_3) protects the ZnO against Zn^{2+} leaching while maintaining the charge transfer between the surface and the interior of the ZnO.

Heterostructure formation of ZnO with other semiconductor materials (TiO_2, g-C_3N_4, CdS) effectively transfers the photogenerated holes from ZnO to the other semiconductor material and thus suppresses the corrosion.

Additionally, the carbon based hybrids (with graphene, carbon nanotubes etc.) enhance the stability of the ZnO by facilitating fast electron extraction and by reducing the charge accumulation in the ZnO.

The nanostructuring of ZnO into rods, sheets and hierarchical structures provides additional improvements concerning the stability. This is achieved by shortening the distance of charge carriers for their diffusion and by reducing the volume of the bulk recombination. However, the nanoscale ZnO is still vulnerable unless protective or charge mediating components are added.

4. Band Gap Engineering through Doping

In addition to improving the stability of the catalysts, modifications of the electronic structure of the semiconductor have also been investigated, especially in terms of extending the absorption range of the photocatalysts towards the visible region. For this purpose, several researchers have used doping to modify the electronic structure of the semiconductor. The objective is to allow the semiconductor to absorb visible light (which represents 43 % of solar irradiance, as opposed to UV irradiance, representing 5%), by introducing impurities in the semiconductor. This is illustrated in Figure 2.1, which shows the effect of the bandgap modification in pure and doped semiconductors, by introducing impurity energy levels, which enables visible light excitation by narrowing the effective band gap.

4.1 Metal Ion Doping

Transition metal dopants like Fe^{3+}, Cr^{3+}, Mn^{2+}, and V^{5+} create discrete levels within the band gap of TiO_2. The dopant states can be used as charge carrier traps that increase visible light absorption and decrease recombination, but over-dopant metal can form recombination centers that reduce photocatalytic activity.

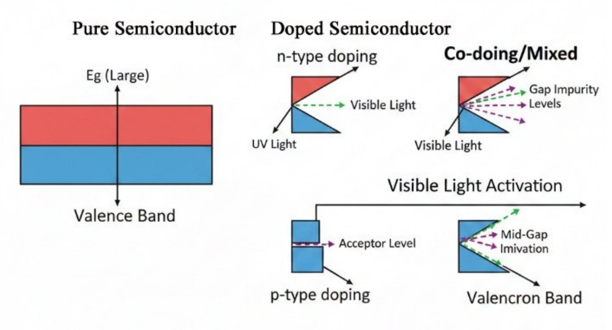

Fig 1: Band gap modification in pure and doped semiconductors, highlighting the role of impurity levels in visible-light activation.

The effectiveness of transition metal dopant is directly related to dopant concentration, oxidation state, and the lattice substitution site. An optimal dopant concentration will cause the dopant ions to replace Ti^{4+} ions at the lattice site, creating shallow trap states that will temporally hold photogenerated electrons or holes and prolong charge carrier lifetime and facilitate redox reactions at the interface. For example, Fe^{3+} ions can cycle between Fe^{3+}/Fe^{2+} states, acting as electron mediators to improve the oxygen reduction reaction on the surface of the catalyst.

However, excess metal loading produces deep level trap states that function as nonradiative recombination centers and accelerate the electron-hole recombination. Excessive metal incorporation can also produce lattice distortion, phase segregation, or secondary oxide cluster formation that degrade light absorption homogeneity and surface reactivity.

Additionally, metal ion doped TiO_2 suffers from poor thermal and photochemical stability. Upon extended illumination, some dopant ions can migrate to the surface or undergo oxidation-reduction cycling that changes the local electronic structure and gradually reduces the photocatalytic activity. Some metal ions can also catalyze undesirable back reactions or participate in parasitic charge recombination pathways.

Therefore, researchers now focus on developing controlled doping techniques such as low level doping, gradient doping, and co-doping with nonmetallic elements to achieve a balance between increased visible light activation and reduced structural degradation. If properly designed, transition metal doped TiO_2 represents a viable approach for improving the efficiency of solar driven photocatalytic reactions while achieving acceptable long-term performance.

4.2 Nonmetal Doping

Nonmetal dopants such as nitrogen, sulfur, carbon, and boron represent a more effective means of decreasing the band gap width of TiO_2 and subsequently increasing visible light absorption, relative to transition metal dopants. Nitrogen doped TiO_2 has demonstrated superior visible light absorption characteristics due to hybridization of the N 2p and O 2p orbitals, and therefore has been identified as one of the best performing visible light absorbing photocatalysts to date [8].

The advantages of using nonmetallic dopants stem from their ability to modify the valence band edge rather than introduce deep mid-gap states that are typically introduced by transition metal dopants. In nitrogen doped TiO_2, substitutional nitrogen replaces lattice oxygen, and as a result, the valence band edge is shifted upwards while the conduction band edge remains unchanged. Therefore, the modified band structure allows for excitation by visible light while retaining enough redox potential for oxidative and reductive reactions.

Similar mechanisms operate for sulfur doped TiO_2 where S 3p orbitals contribute to broadening of the valence band. Depending upon the synthesis conditions, sulfur can exist as either S^{2-} or S^{6+}, thus affecting both the optical properties and charge carrier dynamics. Carbon doped TiO_2 can occur through substitutional or interstitial incorporation of C atoms, forming localized states near the valence band or within the bandgap. Moderate carbon doping increases visible light absorption; however, excessive incorporation of carbon can form recombination centers.

Boron doped TiO_2 provides enhanced surface acidity and improved adsorption of organic contaminants, thereby indirectly enhancing photocatalytic activity. Boron differs from nitrogen and sulfur in that it primarily affects surface electronic states and defect chemistry and not the bulk bandgap width. Importantly, nonmetallic doping improves photochemical stability because nonmetallic dopants do not undergo redox cycling upon illumination, and therefore doped systems exhibit better resistance to photocorrosion and dopant leaching. Co-doping strategies – e.g., N-C or N-S co-doped TiO_2 — have been found to provide synergistic benefits by simultaneously enhancing light absorption and charge separation efficiency.

Collectively, nonmetallic doping presents a versatile and scalable method for extending the photoresponsivity of wide bandgap semiconductors into the visible range, while minimizing recombination losses, allowing for efficient solar driven photocatalytic applications.

5. Carbon Based Photocatalytic Composite Materials

5.1 Graphene and Graphene Oxide

Graphene and its derivatives (graphene oxide and reduced graphene oxide) have dramatically affected the development of photocatalysts, owing to the exceptional electrical conductivity, large surface areas, and rapid electron mobility exhibited by these materials. Graphene functions as an electron collector when paired with semiconductors, rapidly collecting and transporting photogenerated electrons and thus inhibiting recombination [9].

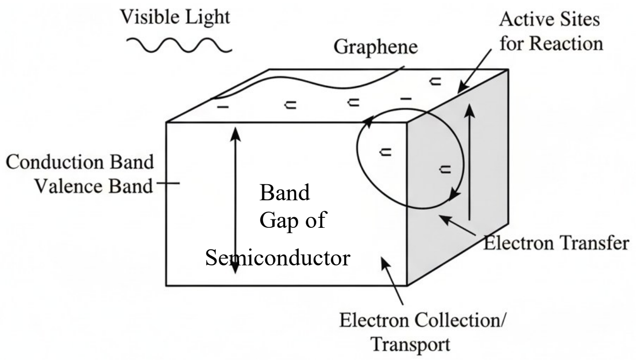

Fig 2: Depicts the charge transfer mechanism in graphene–semiconductor composites.

Carbon nanotubes provide a single-dimensional conductive pathway to allow for directional electron transport. The addition of carbon nanotubes to TiO_2 has produced significantly greater dye, pharmaceutical and pesticide degradations than seen in standard TiO_2 systems. As molecular electron acceptors, fullerenes (C_{60}) have a very high electron affinity allowing them to act as additional agents to assist in charge separation.

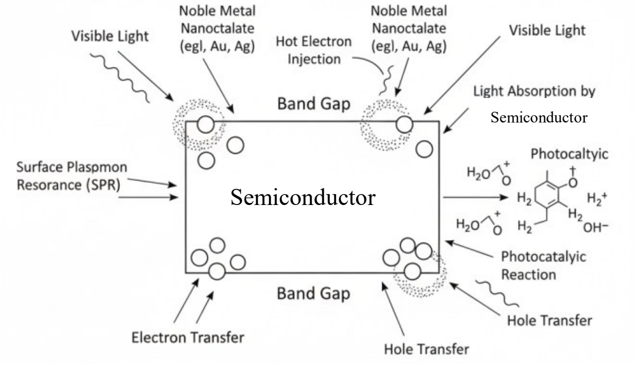

Fig. 3: SPR-enhanced photocatalysis in noble metal-decorated nanostructures.

6. Nanomaterials and Size Effect

Nanostructuring of photocatalysts offers several distinct benefits over their bulk counterparts including, an increase in surface area, decreased length of charge diffusion, and ability to tune electronic properties.

These include; zero dimensional nanoparticles, one-dimensional nanorods, two-dimensional nanosheets, and three-dimensional hierarchical structures.

Quantum size effects may allow band-edge position modification in very small nanoparticles through tailoring of redox potential. However, aggregation of nano-particles and the retrieval of nano-particles are significant practical issues.

7. Advanced Heterojunction Architectures

Construction of heterojunctions constitutes one of the most effective ways to increase photo-catalytic efficiency.

- For Type II hetero-junctions, electron-hole pairs are separated spatially between two semi-conductors.
- Z-scheme systems maintain a strong redox capability, due to their similarity to the mechanism of photosynthesis found in nature.
- S-scheme hetero-junctions employ both internal electric fields and band-bending to facilitate optimal charge transfer with high redox potentials [11].

8. Plasmonic Photocatalysts

Surface plasmon resonance (SPR) of noble metal particles, such as Au, Ag and Pt generate highly localized electromagnetic fields when excited by visible light. These plasmonic effects improve photo-catalytic performance by increasing light absorption, generating "hot" electron injections and enhancing interfacial charge transfers [12].

9. Magnetic Ferrites and Recoverable Photocatalysts

Spinel ferrites (MFe_2O_4; M = Co, Ni, Zn, Mn) provide visible light sensitivity with magnetic properties that enable easy catalyst recovery using an external magnetic field. This combined property provides a solution to one of the most important obstacles to the wide-scale use of photo-catalysts [13].

10. Emerging Photocatalytic Materials

10.1 Graphitic Carbon Nitride (g-C_3N_4)
Graphitic carbon nitride (g-C_3N_4) is a metal free polymeric semiconductor with a relatively moderate bandgap (approximately 2.7eV). g-C_3N_4 exhibits a strong visible light response and high temperature stability. Additionally, the layered structure of g-C_3N_4 enables simple exfoliation and heterojunction formation [14].

10.2 Metal–Organic Frameworks (MOFs)
Metal-organic frameworks (MOFs) have been shown to have a potentially unlimited surface area and tunable pore sizes, allowing for efficient adsorption-photocatalysis coupling. However, MOFs' instability in water and under irradiation conditions needs further improvement [15].

10.3 Perovskite-Based Photocatalysts
Perovskite oxides and halides possess outstanding optoelectronic properties, including internal polarization fields that facilitate charge separation. However, perovskite-based photocatalysts require additional studies to achieve stable performance under environmental conditions [16].

11. Synthesis Methods and Scalability

Photocatalyst performance is significantly influenced by the synthesis method employed, including sol-gel, hydrothermal, solvothermal, combustion and chemical vapor deposition. Scale-up of laboratory synthesis to industrial scale is a major problem and includes the preservation of structural uniformity and cost effectiveness [17].

12. Conclusion

Research into photocatalytic materials has moved from the empirical identification of active photocatalytic materials to the rational design of materials based on interfaces. Future advances in this field are anticipated to be focused on development of multi-functional composites that integrate light absorption, charge separation, catalytic activity and recovery in a single material system. It is also anticipated that the integration of nanotechnology, computer simulations and reactor engineering will accelerate the development of photocatalysis from laboratory demonstrations to real world solutions for environmental and energy applications.

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