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**Recent Advances in Crystal Defect Engineering of Semiconductor
Photocatalysts for Sustainable Environmental and Energy Applications**

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Abstract

Semiconductor photocatalysis has emerged as one of the most promising green technologies for addressing environmental pollution and global energy challenges through solar energy utilization. Nevertheless, the practical application of conventional semiconductor photocatalysts is often limited by their narrow visible-light absorption, rapid recombination of photogenerated electron-hole pairs, insufficient active sites, and poor charge-transfer efficiency. Defect engineering has recently attracted significant attention as an effective strategy to overcome these limitations by deliberately introducing structural imperfections into semiconductor materials. These defects, including oxygen vacancies, sulphur vacancies, nitrogen vacancies, metal vacancies, interstitial defects, antisite defects, grain boundaries, and dislocations, profoundly modify the electronic structure, surface chemistry, and catalytic properties of photocatalysts. Properly engineered defects create localized energy states within the bandgap, enhance visible-light absorption, facilitate efficient charge separation, improve carrier mobility, and provide abundant catalytic active sites, thereby significantly enhancing photocatalytic performance. Various synthesis approaches such as thermal reduction, plasma treatment, ion implantation, chemical etching, hydrothermal synthesis, solvothermal processing, hydrogenation, and laser irradiation have been developed to precisely regulate defect concentration and distribution. Advanced characterization techniques, including electron paramagnetic resonance spectroscopy-ray photoelectron spectroscopy, photoluminescence spectroscopy, Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, and X-ray diffraction, are extensively employed to investigate defect structures and their influence on photocatalytic behaviour. This review comprehensively discusses the principles of semiconductor photocatalysis, defect engineering strategies, defect characterization methods, and the role of defects in enhancing photocatalytic activity. Furthermore, recent advances in defect-engineered photocatalysts, including titanium dioxide, zinc oxide, graphitic carbon nitride, bismuth vanadate, tungsten trioxide, cadmium sulphide, and other emerging semiconductor systems, are summarized. Finally, current challenges, future research directions, and opportunities for designing next-generation high-performance photocatalysts for environmental remediation and sustainable solar energy conversion are critically discussed.

Keywords: Semiconductor photocatalysis; Defect engineering; Oxygen vacancies; Crystal defects; Charge separation; Visible-light photocatalysis; Surface defects; Bandgap

engineering; Environmental remediation; Solar energy conversion; Nanomaterials; Photocatalytic degradation.

1. Introduction

The rapid growth of industrialization, urbanization, and population has resulted in severe environmental pollution and an increasing global demand for sustainable energy resources [1]. Wastewater contaminated with organic dyes, pharmaceutical residues, pesticides, heavy metals, and various emerging pollutants poses serious threats to ecosystems and human health. Simultaneously, the depletion of fossil fuels and the associated emission of greenhouse gases have intensified the search for environmentally friendly technologies capable of harnessing renewable energy [2-3]. Semiconductor photocatalysis has emerged as a highly promising solution because it utilizes abundant solar energy to drive chemical reactions under mild operating conditions without generating secondary pollution [4].

Since the discovery of photocatalytic water splitting on titanium dioxide electrodes in 1972, semiconductor photocatalysis has received tremendous research attention owing to its potential applications in wastewater treatment, air purification, hydrogen production, carbon dioxide reduction, antibacterial coatings, self-cleaning surfaces, and environmental remediation [5-6]. During photocatalysis, photons with energy equal to or greater than the semiconductor bandgap excite electrons from the valence band to the conduction band, leaving positively charged holes in the valence band. These photogenerated charge carriers subsequently participate in oxidation and reduction reactions to produce highly reactive oxygen species capable of degrading pollutants or driving energy conversion processes [7-8].

Despite remarkable progress, the practical efficiency of conventional semiconductor photocatalysts remains far below theoretical expectations due to several intrinsic limitations [9]. These include rapid recombination of photogenerated electron-hole pairs, limited absorption of visible light, insufficient surface-active sites, poor electrical conductivity, sluggish surface reaction kinetics, and inadequate quantum efficiency [10]. These challenges significantly restrict the large-scale commercialization of photocatalytic technologies [11].

To overcome these limitations, numerous material modification strategies have been proposed, including elemental doping, heterojunction construction, cocatalyst loading, morphology control, plasmonic enhancement, surface sensitization, and defect engineering [12-13]. Among these approaches, defect engineering has recently emerged as one of the most effective and versatile strategies because it enables deliberate manipulation of the crystal structure at the atomic level without fundamentally altering the host semiconductor composition. Carefully introduced defects modify the electronic band structure, create localized energy levels, improve charge separation efficiency, extend visible-light absorption, increase carrier mobility, and generate abundant catalytically active sites [14-15].

Defects in semiconductor materials can be classified into point defects, line defects, planar defects, and volume defects. Point defects, such as oxygen vacancies, metal vacancies, sulphur vacancies, nitrogen vacancies, interstitial atoms, and antisite defects, are particularly important because they strongly influence the electronic and catalytic properties of

photocatalysts [16-17]. Oxygen vacancies, for example, have been widely reported to introduce shallow donor states that enhance visible-light absorption and facilitate electron transport. Similarly, sulphur and nitrogen vacancies in non-oxide semiconductors significantly improve photocatalytic activity by modifying charge distribution and surface adsorption characteristics [18].

Recent advances in synthesis technologies including hydrogenation, thermal reduction, plasma treatment, chemical etching, ion implantation, hydrothermal and solvothermal synthesis, laser irradiation, and electrochemical reduction have enabled precise control over defect concentration, spatial distribution, and stability [19]. Simultaneously, sophisticated characterization techniques such as electron paramagnetic resonance spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, photoluminescence spectroscopy, Raman spectroscopy, positron annihilation spectroscopy, and density functional theory calculations have provided deeper insights into defect formation mechanisms and their influence on photocatalytic performance [20-21].

This article comprehensively reviews the latest developments in defect engineering of semiconductor photocatalysts for enhanced photocatalytic activity [22]. The principles of semiconductor photocatalysis, classifications of crystal defects, defect creation strategies, characterization methods, and the influence of defects on electronic structure and photocatalytic mechanisms are systematically discussed [23-24]. Furthermore, recent progress in defect-engineered titanium dioxide, zinc oxide, graphitic carbon nitride, bismuth vanadate, tungsten trioxide, cadmium sulphide, and other emerging semiconductor photocatalysts is critically analysed. Finally, current challenges, future opportunities, and research directions for designing highly efficient defect-engineered photocatalysts for sustainable environmental and energy applications are highlighted [25].

2. Fundamentals of Semiconductor Photocatalysis

Semiconductor photocatalysis is a light-driven catalytic process in which semiconductor materials absorb photons and convert solar energy into chemical energy to initiate oxidation and reduction reactions. Since the pioneering discovery of photocatalytic water splitting on titanium dioxide, semiconductor photocatalysis has become an important research field for environmental remediation and sustainable energy production [26]. Common semiconductor photocatalysts include TiO_2 , ZnO , WO_3 , BiVO_4 , CdS , Fe_2O_3 , and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$). A semiconductor possesses a filled valence band (VB) and an empty conduction band (CB), separated by an energy gap known as the bandgap (E_g). When incident light with energy equal to or greater than the bandgap strikes the semiconductor surface, electrons are excited from the valence band to the conduction band, leaving positively charged holes in the valence band:



The generated electrons and holes migrate to the catalyst surface, where they participate in reduction and oxidation reactions, respectively [28]. Electrons reduce adsorbed oxygen molecules to generate superoxide radicals ($\text{O}_2^{\bullet-}$), while holes oxidize water or hydroxide ions to produce hydroxyl radicals ($\bullet\text{OH}$). These reactive oxygen species are highly oxidative and effectively decompose organic pollutants into harmless products such as CO_2 and H_2O .

The overall photocatalytic process involves five sequential steps: Absorption of photons by the semiconductor, Generation of electron–hole pairs, Separation and migration of charge carriers, Surface redox reactions with adsorbed species and Mineralization of pollutants or generation of valuable products. The photocatalytic efficiency depends on several factors, including bandgap energy, crystallinity, particle size, morphology, specific surface area, defect density, charge-carrier lifetime, and surface reaction kinetics. However, conventional semiconductor photocatalysts suffer from rapid electron–hole recombination, limited visible-light absorption, insufficient active sites, and low quantum efficiency, which significantly restrict their practical performance. To address these challenges, advanced material engineering strategies such as elemental doping, heterojunction construction, cocatalyst loading, morphology control, and defect engineering have been extensively investigated. Among these approaches, defect engineering has emerged as one of the most effective methods because it enables atomic-scale tuning of the electronic structure while preserving the overall crystal framework [29-30].

3. Concept of Defect Engineering

Defect engineering refers to the deliberate introduction, manipulation, and regulation of structural imperfections within a crystalline semiconductor to optimize its electronic, optical, chemical, and catalytic properties. Unlike conventional crystal defects that naturally occur during material synthesis, engineered defects are intentionally created through controlled synthesis or post-treatment processes. Crystal defects modify the periodic arrangement of atoms and introduce localized electronic states within the semiconductor bandgap. These localized states influence charge-carrier transport, adsorption behaviour, surface reaction kinetics, and light absorption. Properly controlled defect concentrations can significantly improve photocatalytic activity by: Enhancing visible-light absorption through bandgap modification, Increasing the lifetime of photogenerated electrons and holes, promoting efficient charge separation, creating additional catalytic active sites, improving adsorption of reactant molecules, accelerating interfacial charge transfer and Reducing activation energy for surface reactions. Several techniques are commonly employed to engineer defects, including thermal reduction, hydrogen treatment, plasma irradiation, ion implantation, electrochemical reduction, laser irradiation, chemical etching, hydrothermal synthesis, solvothermal synthesis, and mechanical milling. The choice of method determines the type, concentration, and stability of the generated defects. Modern characterization techniques such as electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, positron annihilation spectroscopy (PAS), photoluminescence spectroscopy (PL), high-resolution transmission electron microscopy (HRTEM), and density functional theory (DFT) calculations enable accurate identification and analysis of defect structures. Defect engineering has become a central strategy for designing next-generation photocatalysts capable of utilizing visible light more efficiently while maintaining long-term structural stability and catalytic performance [31-32].

4. Types of Crystal Defects

Crystal defects are imperfections in the periodic arrangement of atoms within a crystal lattice. These defects alter the structural, electrical, optical, and catalytic properties of semiconductor materials. Depending on their dimensionality, crystal defects are generally classified into point defects, line defects, planar defects, and volume defects. Among these, point defects and planar defects play particularly important roles in semiconductor photocatalysis because they directly influence the electronic band structure and surface reaction mechanisms [33].

Types of Crystal Defects in Semiconductor Photocatalysts and Their Influence on Photocatalytic Performance as shown in Figure 1.

TYPES OF CRYSTAL DEFECTS IN SEMICONDUCTOR PHOTOCATALYSTS

Defects tailor electronic structure, promote charge separation, enhance light absorption and create active sites for efficient photocatalytic performance.

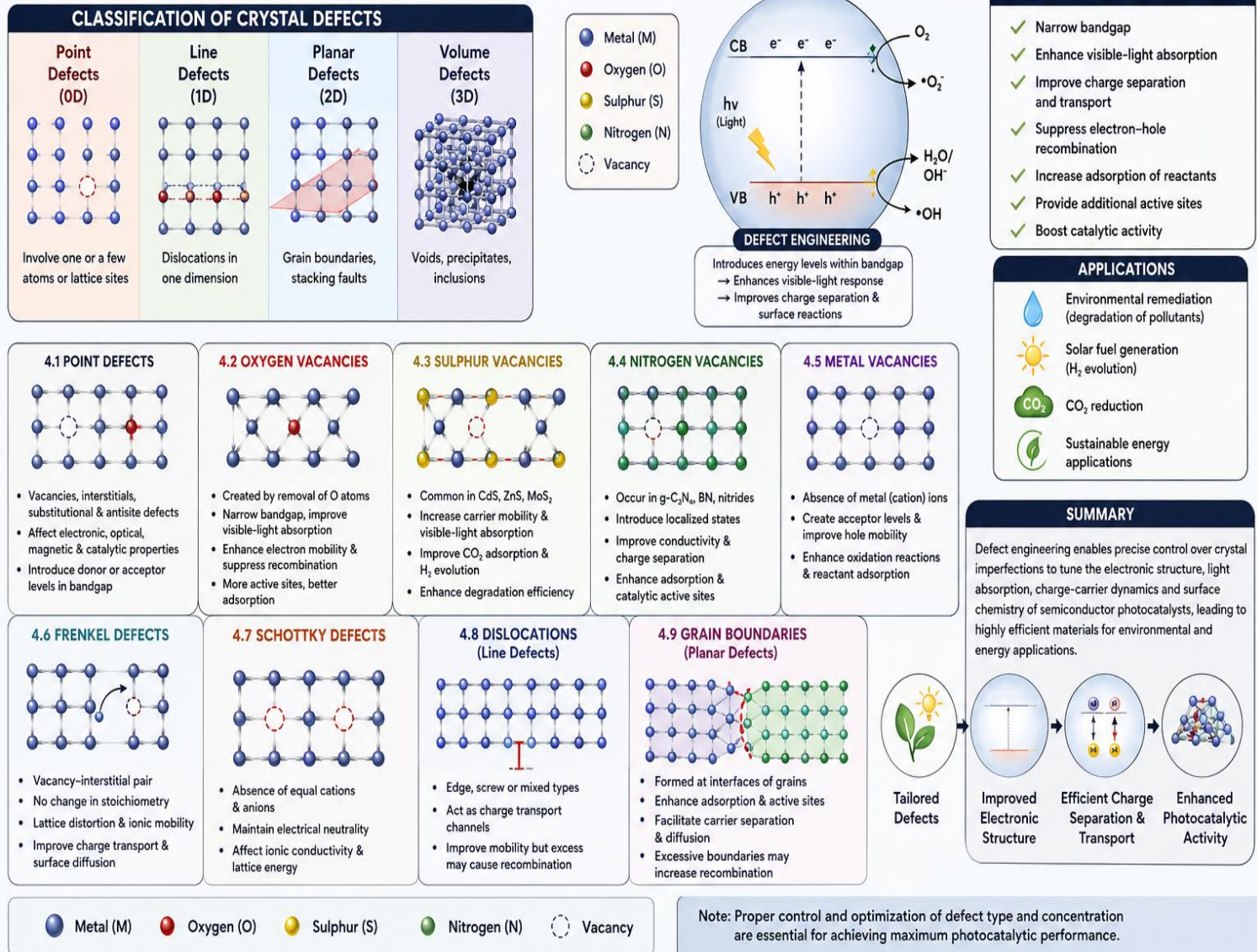


Figure 1: Types of Crystal Defects in Semiconductor Photocatalysts and Their Influence on Photocatalytic Performance

4.1 Point Defects

Point defects are localized atomic-scale imperfections involving one or a few lattice sites. They represent the most common defects in semiconductor photocatalysts and include vacancies, interstitial atoms, substitutional atoms, and antisite defects. Point defects influence numerous material properties, including: Electronic conductivity, Carrier concentration, Optical absorption, Charge separation efficiency, Surface adsorption and Catalytic activity. Controlled introduction of point defects often enhances photocatalytic performance by creating shallow donor or acceptor energy levels within the bandgap, thereby facilitating charge transport and extending visible-light absorption [34].

4.2 Oxygen Vacancies

Oxygen vacancies are among the most extensively studied defects in oxide semiconductor photocatalysts such as TiO_2 , ZnO , WO_3 , CeO_2 , and BiVO_4 . They are created when oxygen atoms are removed from their lattice positions, leaving vacant sites. Oxygen vacancies provide several advantages: Narrow the effective bandgap, improve visible-light absorption, introduce donor energy levels, enhance electron mobility, suppress electron-hole recombination, increase adsorption of oxygen molecules and generate additional catalytic active sites. However, excessive oxygen vacancies may become recombination centers, reducing photocatalytic efficiency. Therefore, optimizing vacancy concentration is crucial for achieving maximum performance [35].

4.3 Sulphur Vacancies

Sulphur vacancies are common in metal sulphide photocatalysts such as CdS , ZnS , and MoS_2 . Removal of sulphur atoms changes the electronic environment surrounding neighbouring metal atoms. Sulphur vacancies contribute to: Increased carrier mobility, Enhanced visible-light absorption, Improved CO_2 adsorption, Faster electron transport, Increased hydrogen evolution activity and Improved photocatalytic degradation efficiency. Recent studies demonstrate that sulphur-vacancy-rich CdS exhibits significantly enhanced hydrogen production under visible-light irradiation [36].

4.4 Nitrogen Vacancies

Nitrogen vacancies mainly occur in graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), boron nitride, and transition-metal nitrides. Nitrogen vacancies produce localized electronic states that: Extend visible-light absorption, improve charge separation, increase electrical conductivity, enhance adsorption of reactants and increase surface-active sites. Nitrogen-deficient $\text{g-C}_3\text{N}_4$ has shown remarkable improvements in photocatalytic hydrogen evolution and degradation of organic contaminants [37].

4.5 Metal Vacancies

Metal vacancies arise when cationic atoms are absent from their lattice positions. Examples include titanium vacancies in TiO_2 , zinc vacancies in ZnO , and bismuth vacancies in BiVO_4 . Metal vacancies can: Produce acceptor energy levels, increase hole mobility, enhance charge separation, improve adsorption of reactants and Promote surface oxidation reactions. Compared with oxygen vacancies, metal vacancies often provide stronger oxidation capability because they facilitate efficient hole transport [38].

4.6 Frenkel Defects

A Frenkel defect consists of a vacancy-interstitial pair in which an atom leaves its normal lattice position and occupies an interstitial site without changing the overall composition. Characteristics include: Preservation of crystal stoichiometry, Formation of lattice distortion, increased ionic mobility, modified electronic structure and Enhanced surface diffusion. Frenkel defects contribute to improved charge transport and may enhance photocatalytic efficiency by increasing defect-assisted charge migration [39].

4.7 Schottky Defects

Schottky defects involve the simultaneous absence of equal numbers of cations and anions from their lattice positions while maintaining electrical neutrality. These defects: Reduce crystal density, increase ionic conductivity, influence carrier diffusion, modify lattice energy and affect adsorption behaviour. Although less common than oxygen vacancies, Schottky defects significantly influence ionic transport in oxide photocatalysts [40].

4.8 Dislocations

Dislocations are one-dimensional line defects resulting from irregular atomic alignment within the crystal lattice. They are categorized into edge dislocations, screw dislocations, and mixed dislocations. Dislocations can: Act as charge transport channels, improve carrier mobility, increase surface roughness, Generate localized strain fields and provide additional catalytic reaction sites. Properly controlled dislocation density can improve photocatalytic activity, whereas excessive dislocations may accelerate charge recombination [41].

4.9 Grain Boundaries

Grain boundaries are planar defects formed at the interfaces between adjacent crystalline grains with different crystallographic orientations. Grain boundaries influence photocatalytic performance by: Enhancing reactant adsorption, providing abundant catalytic active sites, facilitating carrier separation, increasing diffusion pathways, modifying local electronic structures and promoting interfacial charge transfer. Nanocrystalline photocatalysts typically contain numerous grain boundaries that contribute to superior catalytic performance. However, excessive grain boundaries may also introduce recombination centres if not properly controlled. Therefore, optimizing grain size and boundary characteristics is essential for maximizing photocatalytic efficiency. Overall, defect engineering enables precise tailoring of these crystal imperfections to regulate the electronic structure, light absorption, charge-carrier dynamics, and surface chemistry of semiconductor photocatalysts. By understanding the roles of individual defect types and their interactions, researchers can design highly efficient photocatalytic materials for environmental remediation, solar fuel generation, carbon dioxide reduction, and other sustainable energy applications [42-43].

5. Methods for Creating Defects

Defect engineering involves the deliberate introduction of structural imperfections into semiconductor photocatalysts to modify their electronic structure, improve charge-carrier dynamics, and enhance photocatalytic performance. The type, concentration, and distribution of defects are strongly influenced by the synthesis method. Selecting an appropriate defect-generation technique is therefore essential for achieving high photocatalytic efficiency [44].

METHODS FOR CREATING DEFECTS IN SEMICONDUCTOR PHOTOCATALYSTS

Defect engineering techniques introduce structural imperfections that tune the electronic structure, improve charge-carrier dynamics and enhance photocatalytic performance.

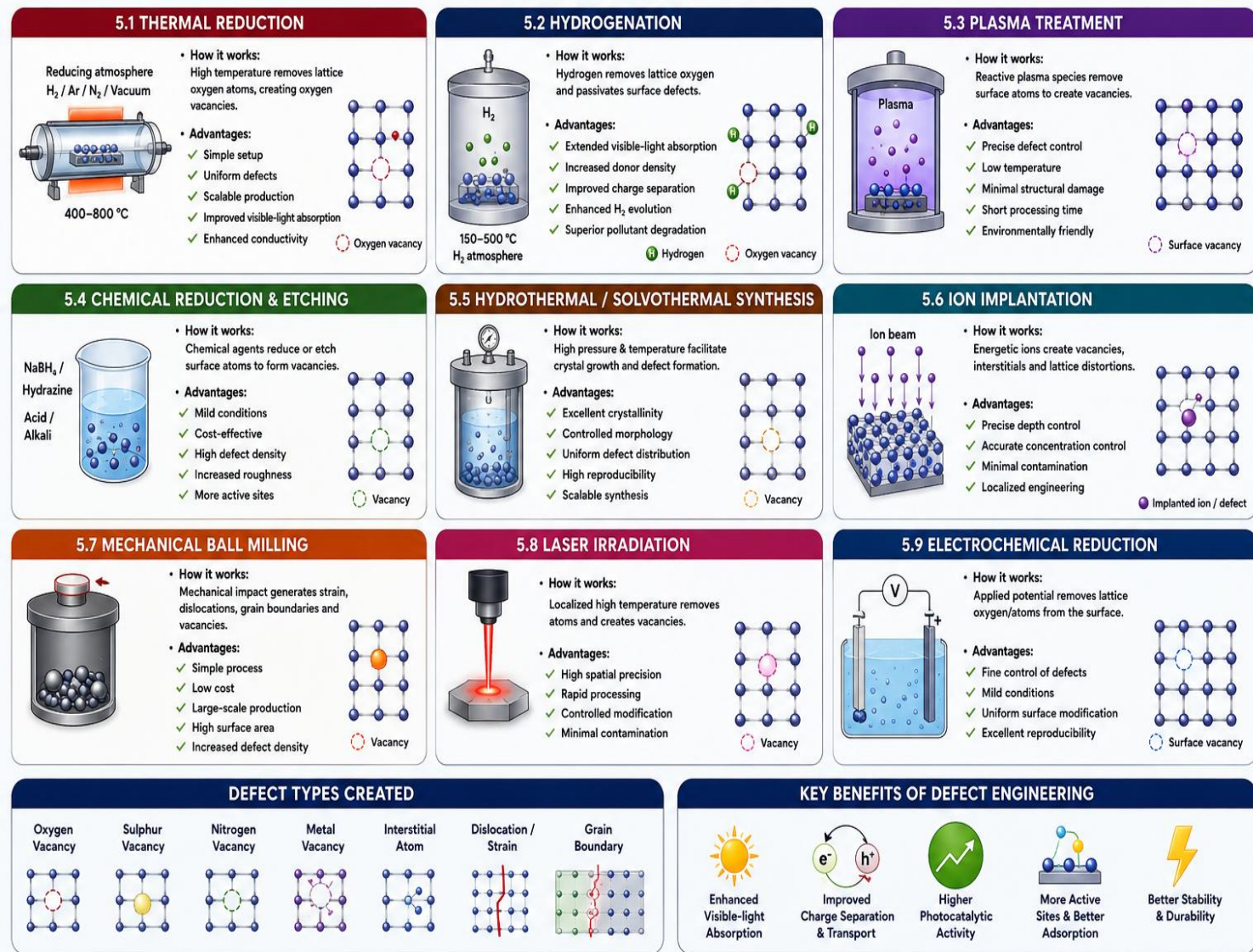


Figure 2: Methods for Creating Crystal Defects in Semiconductor Photocatalysts

5.1 Thermal Reduction

Thermal reduction is one of the simplest and most widely employed methods for producing oxygen-deficient semiconductor photocatalysts. In this approach, semiconductor materials are heated under reducing atmospheres such as hydrogen, argon, nitrogen, or vacuum conditions. Elevated temperatures facilitate the removal of lattice oxygen atoms, generating oxygen vacancies and defect-induced electronic states [45]. Advantages include: Simple experimental setup, Uniform defect formation, Scalable production, improved visible-light absorption and Enhanced electrical conductivity. However, excessive reduction may destabilize the crystal structure or create deep defect states that promote electron–hole recombination [46].

5.2 Hydrogenation

Hydrogenation is a specialized reduction process in which semiconductors are treated with hydrogen gas under controlled temperature and pressure. Hydrogen atoms remove lattice oxygen and create oxygen vacancies while simultaneously passivating undesirable surface defects. Hydrogen-treated photocatalysts often exhibit: Extended visible-light absorption, Increased donor density, Improved charge separation, Enhanced photocatalytic hydrogen evolution, Superior pollutant degradation efficiency. Hydrogenated TiO₂, commonly referred to as "black TiO₂," is a notable example that exhibits significantly enhanced solar-light photocatalytic activity [47].

5.3 Plasma Treatment

Low-temperature plasma provides an effective method for generating surface defects without substantially altering the bulk crystal structure. Reactive plasma species selectively remove lattice atoms, producing oxygen, sulphur, or nitrogen vacancies. Advantages include: Precise control of defect concentration, Low processing temperatures, Minimal structural damage, short processing times and environmentally friendly operation. Plasma treatment has been successfully applied to TiO₂, ZnO, WO₃, and g-C₃N₄ photocatalysts [48].

5.4 Chemical Reduction and Etching

Chemical reducing agents such as sodium borohydride (NaBH₄), hydrazine hydrate, and metal hydrides are frequently used to create vacancies through selective reduction. Chemical etching using acids or alkalis can also remove surface atoms and expose highly active defect-rich facets. Benefits include: Mild reaction conditions, Cost-effectiveness, High defect density, Increased surface roughness and Enhanced catalytic active sites [49].

5.5 Hydrothermal and Solvothermal Synthesis

Hydrothermal and solvothermal methods enable simultaneous crystal growth and defect generation under high-pressure conditions. By adjusting precursor concentration, reaction temperature, pH, solvent composition, and reaction duration, defect density can be carefully controlled. These methods provide: Excellent crystallinity, Controlled particle morphology, Uniform defect distribution, High reproducibility and Large-scale synthesis capability [50].

5.6 Ion Implantation

Ion implantation introduces energetic ions into the semiconductor lattice to generate vacancies, interstitial atoms, and lattice distortions. Implanted ions may also serve as dopants, producing synergistic electronic effects. Advantages include: Precise control over defect depth, Accurate regulation of defect concentration, Minimal contamination, Localized defect engineering. The primary limitation is the requirement for sophisticated instrumentation and relatively high operational costs [51].

5.7 Mechanical Ball Milling

High-energy ball milling induces repeated mechanical deformation, creating lattice strain, dislocations, grain boundaries, and vacancies. This technique offers: Simple processing, Low production cost, Large-scale manufacturing, Enhanced surface area and Increased defect

density. However, prolonged milling may reduce crystallinity and increase amorphization [52].

5.8 Laser Irradiation

Laser irradiation generates localized high temperatures that selectively remove lattice atoms and produce vacancies without affecting the overall crystal morphology. Advantages include: High spatial precision, Rapid processing, Controlled surface modification and Minimal chemical contamination. Laser-induced defect engineering is increasingly employed for advanced photocatalyst fabrication [53].

5.9 Electrochemical Reduction

Electrochemical treatment introduces defects by applying an external electrical potential that removes lattice oxygen or other atoms from the semiconductor surface. Key benefits include: Fine control over defect concentration, Mild operating conditions, Uniform surface modification and Excellent reproducibility. Electrochemical reduction is particularly effective for preparing oxygen-deficient oxide photocatalysts [54].

6. Characterization Techniques

Accurate characterization of crystal defects is essential for understanding their influence on photocatalytic performance. Modern analytical techniques provide structural, chemical, electronic, and optical information about defect-rich semiconductor materials. All Methods for Creating Crystal Defects in Semiconductor Photocatalysts as shown in above figure 2.

6.1 X-ray Diffraction (XRD)

XRD identifies crystal phases, lattice parameters, crystallinity, and structural distortions associated with defect formation. Peak broadening and slight peak shifts often indicate lattice strain and defect generation. Information obtained: Crystal structure, Phase purity. Lattice expansion or contraction and Crystallite size [55].

6.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is one of the most powerful techniques for identifying surface defects and determining the oxidation states of constituent elements. Changes in binding energies reveal the presence of oxygen vacancies, sulphur vacancies, and metal vacancies. Applications: Surface elemental composition, Chemical bonding, Oxidation states, Vacancy identification and Surface stoichiometry.

6.3 Electron Paramagnetic Resonance (EPR)

EPR directly detects unpaired electrons associated with vacancies and paramagnetic defect centers. It is regarded as one of the most reliable methods for identifying oxygen vacancies in oxide semiconductors. Advantages: Direct vacancy detection, High sensitivity, Quantitative defect analysis, Identification of radical species [56-57].

6.4 Photoluminescence Spectroscopy (PL)

PL evaluates the recombination behaviour of photogenerated electron–hole pairs. Lower PL intensity generally indicates more efficient charge separation due to defect-assisted carrier migration. PL provides information on: Recombination rates, Defect-related emission, Carrier lifetime and Bandgap defects [58].

6.5 UV–Visible Diffuse Reflectance Spectroscopy (UV–Vis DRS)

UV–Vis DRS measures optical absorption characteristics and bandgap energy. Defect-rich photocatalysts usually exhibit enhanced visible-light absorption owing to defect-induced intermediate energy levels. Measured properties: Optical bandgap, Light absorption range, Band-edge shifts and Visible-light response [59].

6.6 Raman Spectroscopy

Raman spectroscopy detects lattice vibrations and crystal disorder. Peak shifts, broadening, or intensity changes indicate defect formation and structural distortion. Applications: Crystal disorder, Lattice defects, Phase transitions and Surface structural changes.

6.7 Scanning Electron Microscopy (SEM)

SEM reveals particle morphology, grain structure, and surface texture. Defect-rich materials often exhibit rougher surfaces and increased porosity. Information obtained: Surface morphology, Particle size, Grain distribution and Surface defects [60].

6.8 Transmission Electron Microscopy (TEM)

TEM and High-Resolution TEM provide direct visualization of crystal lattices, dislocations, grain boundaries, and vacancy clusters. Capabilities: Atomic-resolution imaging, Lattice spacing measurement, Grain-boundary observation and Dislocation visualization.

6.9 Brunauer–Emmett–Teller (BET) Surface Area Analysis

BET analysis measures specific surface area and pore-size distribution. Increased defect density often correlates with higher surface area and enhanced adsorption capacity [61-62].

6.9 Density Functional Theory (DFT)

Although computational rather than experimental, DFT has become indispensable for investigating defect formation energies, electronic structures, adsorption mechanisms, and charge distribution. DFT predicts: Defect stability, Band structure, Charge density, Reaction pathways and Photocatalytic mechanisms [63-65] . Characterization Techniques Used for Crystal Defect Analysis in Photocatalysts as shown in Table 1.

Table 1: Characterization Techniques Used for Crystal Defect Analysis in Photocatalysts

Characterization Technique	Principle	Information Obtained / Applications
X-ray Diffraction (XRD)	Determines crystal structure by diffraction of X-rays from crystal planes.	Crystal structure, phase purity, lattice parameters, crystallinity, lattice expansion/contraction, crystallite size, structural distortion, lattice strain, defect generation.
X-ray Photoelectron Spectroscopy (XPS)	Measures binding energies of photoemitted electrons from the material surface.	Surface elemental composition, chemical bonding, oxidation states, oxygen/Sulphur/metal vacancy identification, surface stoichiometry.
Electron Paramagnetic Resonance (EPR)	Detects unpaired electrons associated with paramagnetic defects.	Direct detection of oxygen vacancies, defect centers, radical species, quantitative defect analysis, high sensitivity.
Photoluminescence Spectroscopy (PL)	Measures light emitted from electron–hole recombination after photoexcitation.	Charge-carrier recombination rate, defect-related emission, carrier lifetime, bandgap defects, charge separation efficiency.
UV–Visible Diffuse Reflectance Spectroscopy (UV–Vis DRS)	Evaluates optical absorption and diffuse reflectance of semiconductor materials.	Optical bandgap, light absorption range, band-edge shifts, visible-light response, defect-induced intermediate energy levels.
Raman Spectroscopy	Detects vibrational modes of crystal lattices using inelastic light scattering.	Crystal disorder, lattice defects, phase transitions, structural distortion, surface structural changes.
Scanning Electron Microscopy (SEM)	Produces high-resolution images using a focused electron beam.	Surface morphology, particle size, grain distribution, surface roughness, porosity, surface defects.
Transmission Electron Microscopy (TEM/HRTEM)	Transmits electrons through ultrathin samples for atomic-scale imaging.	Atomic-resolution imaging, lattice spacing, grain boundaries, dislocations, vacancy clusters, crystal defects.
Brunauer–Emmett–Teller (BET) Surface Area Analysis	Determines surface area through gas adsorption–desorption measurements.	Specific surface area, pore-size distribution, adsorption capacity, porosity, defect-related surface characteristics.
Density Functional Theory (DFT)	Computational method based on quantum mechanics for electronic structure calculations.	Defect formation energy, defect stability, electronic band structure, charge density, adsorption mechanisms, reaction pathways, photocatalytic mechanisms.

7. Effect of Defects on Photocatalytic Activity

Crystal defects profoundly influence the optical, electronic, structural, and catalytic properties of semiconductor photocatalysts. Carefully engineered defects enhance photocatalytic performance by modifying charge-carrier dynamics and surface reaction processes.

7.1 Enhanced Visible-Light Absorption

Defects introduce localized electronic states within the bandgap, enabling absorption of lower-energy photons that are otherwise insufficient to excite electrons. Consequently, defect-engineered photocatalysts exhibit expanded visible-light response and improved solar-energy utilization [66].

7.2 Improved Charge Separation

Rapid recombination of photogenerated electron–hole pairs is one of the principal limitations of semiconductor photocatalysis. Appropriate defect sites temporarily trap electrons or holes, prolonging carrier lifetimes and facilitating efficient charge separation before recombination occurs [67].

7.3 Increased Carrier Mobility

Shallow defect states provide additional pathways for charge transport, reducing electrical resistance and accelerating electron migration from the semiconductor interior to the surface reaction sites.

7.4 Formation of Active Catalytic Sites

Vacancies and lattice distortions create unsaturated coordination sites that strongly adsorb reactant molecules such as oxygen, water, carbon dioxide, and organic pollutants. These sites serve as highly active centers for photocatalytic reactions [68-69].

7.5 Enhanced Generation of Reactive Oxygen Species

Defect-rich photocatalysts facilitate the formation of reactive oxygen species, including hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\text{O}_2^{\bullet-}$), singlet oxygen ($^1\text{O}_2$), and hydrogen peroxide (H_2O_2). These highly reactive intermediates efficiently degrade organic contaminants, inactivate microorganisms, and promote oxidation reactions.

7.6 Improved Surface Adsorption

Surface defects increase adsorption energy by introducing chemically active sites with higher affinity toward reactant molecules. Improved adsorption enhances reaction probability and accelerates photocatalytic conversion.

7.7 Band Structure Modulation

Defects alter the electronic band structure by introducing donor or acceptor energy levels. Controlled bandgap engineering enhances solar-light utilization while maintaining sufficient redox potential for photocatalytic reactions [70].

7.8 Increased Quantum Efficiency

Efficient light absorption, prolonged charge-carrier lifetime, rapid electron transport, and enhanced surface reaction kinetics collectively improve the apparent quantum efficiency of defect-engineered photocatalysts [71].

7.9 Potential Adverse Effects of Excessive Defects

Although moderate defect concentrations improve photocatalytic activity, excessive defects may become deep trap states that accelerate electron–hole recombination, reduce crystallinity, impair structural stability, and diminish long-term catalytic performance. Therefore, precise regulation of defect type, density, and distribution is essential for maximizing photocatalytic efficiency. Overall, defect engineering has emerged as one of the most effective approaches for tailoring semiconductor photocatalysts at the atomic level [72–73]. By optimizing defect structures through controlled synthesis and comprehensive characterization, researchers can significantly enhance light harvesting, charge separation, surface reactivity, and catalytic efficiency, enabling the development of advanced photocatalysts for environmental remediation, water splitting, carbon dioxide reduction, and sustainable solar energy conversion [74].

8. Defect Engineering in Various Semiconductor Photocatalysts

Defect engineering has become one of the most effective strategies for improving the photocatalytic performance of semiconductor materials. By deliberately introducing vacancies, interstitial atoms, dislocations, grain boundaries, and other structural imperfections, researchers can tailor the electronic structure, enhance visible-light absorption, suppress charge-carrier recombination, and increase the number of catalytically active surface sites [75]. Different semiconductor photocatalysts respond uniquely to defect engineering because of differences in their crystal structures, electronic configurations, and bandgap energies. The following sections summarize recent advances in defect engineering for major semiconductor. Defect Engineering in Various Semiconductor Photocatalysts for Enhanced Photocatalytic Performance photocatalysts as shown in Figure 3. [76].

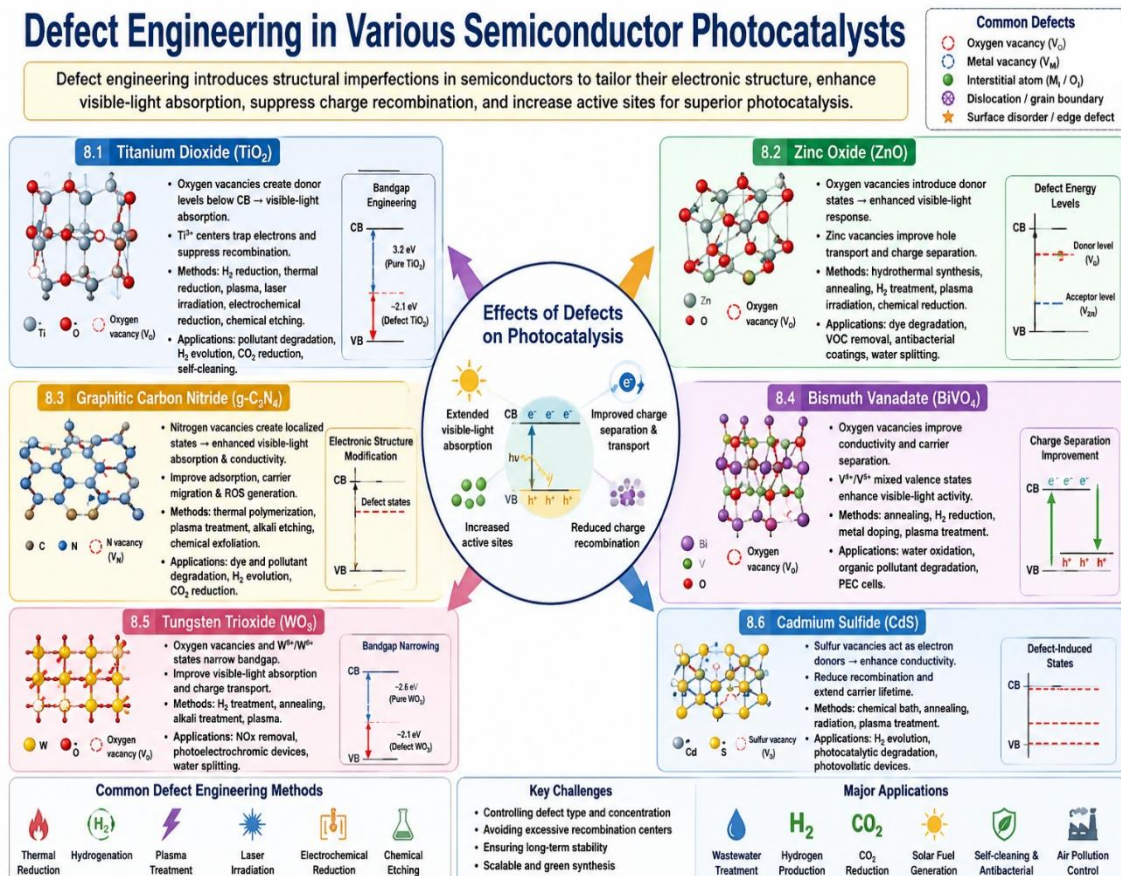


Figure 3: Defect Engineering in Various Semiconductor Photocatalysts for Enhanced Photocatalytic Performance

8.1 Titanium Dioxide (TiO₂)

Titanium dioxide (TiO₂) is the most extensively investigated semiconductor photocatalyst owing to its excellent chemical stability, non-toxicity, low cost, and strong oxidation capability. However, its relatively wide bandgap (3.0–3.2 eV) restricts light absorption primarily to the ultraviolet region, which constitutes only a small fraction of the solar spectrum. Moreover, the rapid recombination of photogenerated electron–hole pairs limit its photocatalytic efficiency. Defect engineering has significantly enhanced the photocatalytic properties of TiO₂ by introducing oxygen vacancies, titanium vacancies, Ti³⁺ centres, and surface disorder. Oxygen vacancies are particularly important because they create donor energy levels below the conduction band, facilitating visible-light absorption and improving charge transport. Ti³⁺ defects generated during hydrogen reduction act as electron-trapping centres that suppress charge recombination and increase the lifetime of photogenerated carriers [77]. Hydrogenated TiO₂, commonly known as black TiO₂, has attracted considerable attention due to its extended absorption from the ultraviolet to the visible and near-infrared regions. Black TiO₂ exhibits superior photocatalytic performance in hydrogen evolution, pollutant degradation, carbon dioxide reduction, and self-cleaning applications. Various defect-generation methods have been employed for TiO₂, including thermal reduction, hydrogenation, plasma treatment, laser irradiation, electrochemical reduction, and chemical etching [78–79]. Advanced characterization techniques such as electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM) confirm the successful formation of oxygen vacancies and Ti³⁺ defect states. Recent studies demonstrate that defect-engineered TiO₂ exhibits enhanced degradation of dyes, antibiotics, pharmaceuticals, and other organic pollutants, together with improved hydrogen production under simulated solar irradiation. However, excessive oxygen vacancies may function as recombination centers, emphasizing the importance of carefully controlling defect concentration [80].

8.2 Zinc Oxide (ZnO)

Zinc oxide (ZnO) is another widely studied semiconductor photocatalyst because of its high electron mobility, low toxicity, abundance, and strong ultraviolet-light absorption. Similar to TiO₂, ZnO possesses a wide bandgap (~3.37 eV), limiting its utilization of visible light. Defect engineering has been extensively applied to ZnO by introducing oxygen vacancies, zinc vacancies, zinc interstitials, and lattice strain. Oxygen vacancies enhance visible-light absorption by introducing donor states within the bandgap, while zinc vacancies function as shallow acceptors that improve hole transport and promote charge separation. Hydrothermal synthesis, thermal annealing, hydrogen treatment, plasma irradiation, and chemical reduction are commonly employed to generate defect-rich ZnO nanostructures [81–82]. Oxygen-deficient ZnO exhibits increased adsorption of oxygen molecules and accelerated formation of reactive oxygen species, including hydroxyl radicals and superoxide radicals, resulting in significantly improved photocatalytic degradation of dyes and emerging contaminants. Nanostructured ZnO containing engineered grain boundaries and dislocations further enhances carrier migration by shortening diffusion distances and providing additional active reaction sites. Defect-engineered ZnO has demonstrated excellent photocatalytic performance

in wastewater treatment, antibacterial coatings, volatile organic compound degradation, and photoelectrochemical water splitting. Despite these advantages, ZnO is susceptible to photo corrosion under prolonged irradiation. Combining defect engineering with surface passivation or heterojunction formation has proven effective in improving its long-term stability [83].

8.3 Graphitic Carbon Nitride (g-C₃N₄)

Graphitic carbon nitride (g-C₃N₄) has emerged as one of the most promising metal-free photocatalysts because of its moderate bandgap (~2.7 eV), visible-light activity, excellent thermal stability, and low-cost synthesis from nitrogen-rich precursors. Nevertheless, pristine g-C₃N₄ suffers from limited surface area, inadequate charge separation, and relatively low photocatalytic efficiency. Nitrogen-vacancy engineering has become a highly effective strategy for overcoming these limitations. Nitrogen vacancies modify the electronic structure of g-C₃N₄ by introducing localized defect states that enhance visible-light absorption and improve electrical conductivity [84]. These vacancies also increase the adsorption of reactant molecules, promote carrier migration, and facilitate the generation of reactive oxygen species. Carbon vacancies, amino defects, and edge defects have also been introduced through thermal polymerization, plasma treatment, alkali etching, and chemical exfoliation. Defect-rich ultrathin g-C₃N₄ nanosheets exhibit significantly enhanced photocatalytic degradation of dyes, hydrogen evolution, carbon dioxide reduction, nitrogen fixation, and antibacterial activity. Combining vacancy engineering with heterojunction construction and cocatalyst deposition has further improved solar-to-chemical energy conversion efficiency, making g-C₃N₄ one of the most attractive photocatalysts for sustainable energy applications [85].

8.4 Bismuth Vanadate (BiVO₄)

Bismuth vanadate (BiVO₄) is a visible-light-responsive semiconductor with a bandgap of approximately 2.4 eV and has attracted widespread attention for photoelectrochemical water oxidation and environmental remediation. Although BiVO₄ absorbs visible light efficiently, its photocatalytic performance is limited by poor charge mobility and rapid recombination of photogenerated carriers. Defect engineering has substantially improved the performance of BiVO₄ by introducing oxygen vacancies, bismuth vacancies, vanadium vacancies, and lattice distortions. Oxygen vacancies increase electrical conductivity by generating donor states that facilitate electron transport and improve visible-light absorption. Bismuth vacancies have been shown to enhance hole transport and promote surface oxidation reactions. Controlled oxygen-vacancy formation also improves water adsorption and accelerates oxygen evolution kinetics during photoelectrochemical water splitting. Hydrothermal synthesis, electrochemical reduction, thermal annealing, and plasma treatment are commonly employed to create defect-rich BiVO₄ nanostructures. Advanced characterization techniques reveal that moderate oxygen-vacancy concentrations effectively suppress charge recombination while preserving crystal stability. Defect-engineered BiVO₄ has demonstrated remarkable improvements in dye degradation, photocatalytic water oxidation, photoelectrochemical hydrogen generation, and carbon dioxide conversion [86].

8.5 Tungsten Trioxide (WO₃)

Tungsten trioxide (WO₃) is a visible-light-active semiconductor with a bandgap ranging from 2.5 to 2.8 eV. Its excellent chemical stability and favourable valence-band position make it suitable for photoelectrochemical oxidation and environmental purification. However, the conduction-band potential of WO₃ is insufficient for efficient hydrogen evolution, and

electron–hole recombination remains a major limitation. Oxygen-vacancy engineering has proven highly effective in improving the photocatalytic properties of WO_3 . Oxygen vacancies generate donor levels within the bandgap, increase electrical conductivity, and promote visible-light absorption [87]. Defect-rich WO_3 nanostructures prepared through hydrogen reduction, thermal annealing, plasma treatment, and electrochemical methods exhibit significantly enhanced photocurrent density and improved degradation of organic contaminants. Surface oxygen vacancies also facilitate adsorption of water molecules and dissolved oxygen, thereby accelerating the generation of hydroxyl radicals and superoxide radicals. Furthermore, combining oxygen-vacancy engineering with heterojunction formation and cocatalyst deposition has markedly improved charge separation efficiency and photocatalytic stability, making WO_3 a promising material for solar energy conversion [88].

8.6 Cadmium Sulfide (CdS)

Cadmium sulphide (CdS) is an important visible-light-responsive semiconductor with a narrow bandgap of approximately 2.4 eV, enabling efficient utilization of solar radiation. It has been widely investigated for photocatalytic hydrogen production and environmental remediation. The major limitation of CdS is severe photo corrosion and rapid recombination of photogenerated carriers. Defect engineering has become an effective strategy to improve both photocatalytic activity and stability. Sulphur vacancies are the most common engineered defects in CdS. These vacancies introduce shallow donor states that facilitate charge separation, increase carrier mobility, and improve visible-light absorption. Sulphur-deficient CdS exhibits enhanced hydrogen evolution rates and improved degradation efficiency toward dyes, pharmaceuticals, and persistent organic pollutants [89]. Cadmium vacancies have also been reported to improve hole mobility and promote surface oxidation reactions. Various synthesis methods, including solvothermal synthesis, thermal reduction, plasma treatment, ion irradiation, and chemical etching, have been successfully employed to generate controlled Sulphur-vacancy concentrations. To overcome photo corrosion, defect-engineered CdS is frequently integrated with cocatalysts, protective shells, or heterojunction partners such as TiO_2 , ZnO , MoS_2 , and graphitic carbon nitride. These composite systems significantly suppress charge recombination and improve long-term photocatalytic stability. Overall, Sulphur-vacancy engineering has transformed CdS into one of the most efficient visible-light photocatalysts for hydrogen evolution and environmental applications. In summary, defect engineering has become a universal strategy for enhancing the performance of semiconductor photocatalysts. Oxygen vacancies dominate oxide semiconductors such as TiO_2 , ZnO , BiVO_4 , and WO_3 , whereas Sulphur and nitrogen vacancies play pivotal roles in CdS and $\text{g-C}_3\text{N}_4$, respectively. By carefully controlling defect type, concentration, and spatial distribution through advanced synthesis techniques, researchers can optimize light harvesting, charge separation, surface reactivity, and catalytic stability. Continued integration of defect engineering with nanostructure design, heterojunction fabrication, cocatalyst loading, and computational materials engineering is expected to accelerate the development of next-generation photocatalysts for environmental remediation, solar fuel production, and sustainable energy conversion [90].

9. Applications of Defect-Engineered Semiconductor Photocatalysts

Defect engineering has significantly expanded the practical applications of semiconductor photocatalysts by improving light absorption, charge-carrier separation, catalytic activity, and long-term stability. These advancements have enabled efficient utilization of solar energy for

environmental protection, renewable energy generation, and sustainable chemical production [91].

9.1 Environmental Remediation

One of the most important applications of defect-engineered photocatalysts is the degradation of environmental pollutants. Oxygen vacancies, sulphur vacancies, and nitrogen vacancies create highly active surface sites that facilitate the generation of reactive oxygen species (ROS), including hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\text{O}_2\bullet^-$) and singlet oxygen ($^1\text{O}_2$). These reactive species efficiently oxidize organic contaminants into harmless products such as carbon dioxide and water. Defect-engineered photocatalysts have demonstrated excellent performance in removing: Organic dyes (methylene blue, rhodamine B, methyl orange) Pharmaceutical residues, Antibiotics, Pesticides, Phenolic compounds, Endocrine-disrupting chemicals and Volatile organic compounds (VOCs). Their superior degradation efficiency, even under visible-light irradiation, makes them attractive for advanced wastewater treatment technologies.

9.2 Photocatalytic Water Splitting for Hydrogen Production

Solar-driven water splitting represents a promising approach for producing clean hydrogen fuel. Defect engineering enhances hydrogen evolution by increasing visible-light absorption, improving charge separation, and lowering the activation energy of surface reactions. Oxygen-deficient TiO_2 , sulphur-vacancy-rich CdS , and nitrogen-deficient $\text{g-C}_3\text{N}_4$ have demonstrated significantly higher hydrogen evolution rates than their pristine counterparts. Integration with cocatalysts such as Pt, Ni, Co, or MoS_2 further improves photocatalytic efficiency by accelerating proton reduction.

9.2 Carbon Dioxide Reduction

The photocatalytic conversion of carbon dioxide into valuable chemicals offers an environmentally friendly strategy for mitigating greenhouse gas emissions while generating renewable fuels. Defect-rich photocatalysts improve CO_2 adsorption through unsaturated coordination sites and facilitate multi-electron transfer processes required for carbon dioxide reduction. Major products include: Carbon monoxide, Methane, Methanol, Formic acid and Ethanol. Oxygen vacancies are particularly effective in activating chemically stable CO_2 molecules and promoting selective reduction pathways.

9.3 Air Purification

Defect-engineered photocatalysts effectively remove airborne pollutants by oxidizing volatile organic compounds, nitrogen oxides, sulphur oxides, and toxic gases under solar irradiation. Applications include: Indoor air purification systems, Self-cleaning building materials, Photocatalytic paints, Air filtration devices and Antibacterial coatings. The continuous generation of reactive oxygen species enables long-term purification without requiring additional chemical reagents.

9.4 Self-Cleaning Surfaces

Photocatalytic coatings containing defect-engineered TiO_2 and ZnO possess self-cleaning properties by decomposing organic contaminants deposited on surfaces. Typical applications

include: Architectural glass, Solar panels, Ceramic tiles, medical devices and Automotive coatings. Improved visible-light activity allows efficient self-cleaning even under natural sunlight.

9.5 Antibacterial and Antiviral Applications

Reactive oxygen species generated by photocatalysts destroy bacterial cell membranes, viral envelopes, proteins, and nucleic acids. Defect-engineered photocatalysts have demonstrated high antimicrobial efficiency against: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, Various pathogenic fungi and several enveloped viruses. Potential applications include hospital disinfection, water sterilization, food packaging, and antimicrobial coatings [92].

9.6 Photoelectrochemical Water Treatment

Defect-rich semiconductor photoelectrodes improve photoelectrochemical oxidation by enhancing charge transport and reducing interfacial resistance. Applications include: Industrial wastewater treatment, Heavy metal removal, Desalination pretreatment and Organic pollutant mineralization

9.7 Sustainable Chemical Synthesis

Photocatalytic systems utilizing defect-engineered semiconductors have shown remarkable capability for green organic synthesis through selective oxidation and reduction reactions under mild conditions. Potential applications include: Selective alcohol oxidation, Organic coupling reactions, Fine chemical synthesis, Nitrogen fixation and Ammonia production [93].

10. Challenges

Despite remarkable progress, several scientific and technological challenges continue to limit the large-scale implementation of defect-engineered semiconductor photocatalysts. Achieving accurate control over defect concentration, type, spatial distribution, and stability remains difficult. Excessive defects often function as charge recombination centres rather than beneficial catalytic sites. Certain defect-rich photocatalysts gradually lose their defect structures during prolonged photocatalytic reactions because of oxidation, lattice reconstruction, or surface healing. Visible-light semiconductors such as CdS suffer severe photo corrosion, limiting their long-term operational stability despite defect engineering. Although modern analytical techniques provide valuable information, accurately quantifying atomic-scale defects remains challenging. Different characterization methods frequently provide complementary rather than identical information. Variations in synthesis parameters often produce different defect concentrations, making reproducibility difficult across laboratories [94]. Most defect-engineering methods remain laboratory-scale techniques. Developing cost-effective industrial synthesis methods with precise defect control is still a major challenge. Although numerous studies reports improved photocatalytic performance, the precise mechanisms by which different defects influence charge transport and surface reactions remain incompletely understood. Commercial photocatalysts require stable defect structures capable of maintaining high catalytic performance over extended operating periods under real environmental conditions [95]. Challenges and Future Perspectives of Defect-Engineered Semiconductor Photocatalysts as shown in Table 2.

Table 2: Challenges and Future Perspectives of Defect-Engineered Semiconductor Photocatalysts

Challenge	Description	Future Perspective / Possible Solution
Precise Defect Control	Accurate control over defect concentration, type, spatial distribution, and stability remains difficult. Excessive defects can act as charge recombination centres rather than active catalytic sites.	Develop advanced synthesis techniques with precise defect engineering and real-time process control to optimize defect concentration.
Structural Stability	Defect-rich photocatalysts may lose their defect structures during prolonged reactions because of oxidation, lattice reconstruction, or surface healing.	Design stable defect configurations through surface passivation, heterostructure formation, and protective coatings.
Photocorrosion	Visible-light-responsive semiconductors such as CdS experience severe photo corrosion, reducing long-term photocatalytic performance.	Improve stability using cocatalysts, protective surface layers, heterojunctions, and alternative corrosion-resistant materials.
Characterization Limitations	Precise quantification of atomic-scale defects remains challenging. Individual characterization techniques often provide complementary rather than complete information.	Integrate advanced in situ/operando characterization techniques with computational modelling for comprehensive defect analysis.
Reproducibility	Small variations in synthesis conditions lead to significant differences in defect concentration and photocatalytic performance across laboratories.	Establish standardized synthesis protocols and characterization procedures to improve reproducibility.
Scale-Up	Most defect-engineering strategies are limited to laboratory-scale synthesis and are difficult to translate into industrial production.	Develop scalable, cost-effective, environmentally friendly, and continuous manufacturing methods suitable for industrial applications.
Mechanistic Understanding	The fundamental mechanisms by which different defects influence charge transport, surface reactions, and catalytic activity remain incompletely understood.	Combine experimental investigations with Density Functional Theory (DFT), machine learning, and operando spectroscopy to reveal defect–activity relationships.
Long-Term Durability	Commercial photocatalysts require defect structures that remain stable under prolonged operation and realistic environmental conditions.	Design highly durable photocatalysts with stable defect architectures and evaluate their long-term performance under practical operating conditions.

11. Future Perspectives

Future research should focus on designing highly efficient, stable, and economically viable defect-engineered photocatalysts through interdisciplinary approaches combining materials science, nanotechnology, computational modelling, and artificial intelligence. Several promising research directions include:

- a) Atomic-level control of defect formation using advanced synthesis technologies.
- b) Integration of defect engineering with heterojunction construction.
- c) Development of dual-defect and multiple-defect systems.
- d) Machine-learning-assisted optimization of defect structures.
- e) Artificial intelligence-guided materials discovery.
- f) In situ and operando characterization during photocatalytic reactions.
- g) Advanced computational simulations using density functional theory and molecular dynamics.
- h) Design of defect-rich single-atom photocatalysts.
- i) Development of flexible and scalable photocatalytic devices.
- j) Commercial-scale fabrication of defect-engineered nanomaterials.
- k) Integration into solar hydrogen production systems.
- l) Large-scale environmental remediation technologies.
- m) Sustainable carbon-neutral fuel production.
- n) Smart photocatalytic reactors for industrial wastewater treatment.

Future investigations should also emphasize environmentally benign synthesis methods, improved defect stability, and standardized characterization protocols to accelerate commercialization.

12. Conclusion

- A. Defect engineering has emerged as one of the most powerful strategies for enhancing the performance of semiconductor photocatalysts by precisely manipulating their crystal structures and electronic properties at the atomic scale. Controlled introduction of oxygen vacancies, sulphur vacancies, nitrogen vacancies, metal vacancies, Frenkel defects, Schottky defects, dislocations, and grain boundaries effectively modify the band structure, improves visible-light absorption, enhances charge-carrier separation, and increases the number of catalytically active sites. These structural modifications significantly improve photocatalytic efficiency in applications such as pollutant degradation, hydrogen evolution, carbon dioxide reduction, air purification, antimicrobial treatment, and sustainable chemical synthesis.
- B. Substantial progress has been achieved in developing advanced defect-generation techniques, including thermal reduction, hydrogenation, plasma treatment, chemical etching, ion implantation, hydrothermal synthesis, and electrochemical reduction. Simultaneously, sophisticated characterization tools such as X-ray photoelectron spectroscopy, electron paramagnetic resonance, transmission electron microscopy, Raman spectroscopy, and density functional theory calculations have provided valuable insights into defect formation mechanisms and their influence on photocatalytic behaviour.
- C. Despite these advances, challenges remain in achieving precise defect control, maintaining structural stability, improving reproducibility, and scaling up laboratory synthesis methods for industrial production. Excessive defect concentrations may act

as recombination centres, highlighting the importance of optimizing defect type, density, and distribution for maximum photocatalytic performance.

- D. Future developments integrating defect engineering with nanostructure design, heterojunction fabrication, cocatalyst loading, artificial intelligence, machine learning, and computational materials science are expected to accelerate the discovery of next-generation photocatalysts with superior efficiency and durability. Such advances will contribute significantly to renewable energy production, environmental protection, carbon neutrality, and sustainable industrial development. Consequently, defect engineering is anticipated to remain a central research direction in semiconductor photocatalysis, offering transformative opportunities for the development of efficient solar-driven technologies that address global energy and environmental challenges.

Abbreviation	Full Form
AI	Artificial Intelligence
BET	Brunauer–Emmett–Teller
BiVO ₄	Bismuth Vanadate
C ₃ N ₄	Graphitic Carbon Nitride
CB	Conduction Band
CdS	Cadmium Sulfide
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
DFT	Density Functional Theory
DRS	Diffuse Reflectance Spectroscopy
EPR	Electron Paramagnetic Resonance
H ₂	Hydrogen
H ₂ O	Water
H ₂ O ₂	Hydrogen Peroxide
HRTEM	High-Resolution Transmission Electron Microscopy
MO	Methyl Orange
MB	Methylene Blue
NIR	Near-Infrared
O ₂	Oxygen
O ₂ • ⁻	Superoxide Radical
•OH	Hydroxyl Radical
¹ O ₂	Singlet Oxygen
PAS	Positron Annihilation Spectroscopy
PEC	Photoelectrochemical
PL	Photoluminescence
Pt	Platinum
ROS	Reactive Oxygen Species
RhB	Rhodamine B
SEM	Scanning Electron Microscopy

Abbreviation	Full Form
TEM	Transmission Electron Microscopy
Ti ³⁺	Titanium(III) Species
TiO ₂	Titanium Dioxide
UV	Ultraviolet
UV–Vis DRS	Ultraviolet–Visible Diffuse Reflectance Spectroscopy
VB	Valence Band
VOCs	Volatile Organic Compounds
WO ₃	Tungsten Trioxide
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZnO	Zinc Oxide

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