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Review Article

Photo-catalytic Nano-materials Synthesis and Its Application in Environmental Protection, Energy Conversion and Green Chemical Synthesis

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Abstract

This review paper delves into the synthesis and application of photo-catalytic Nano-materials, focusing on their role in environmental protection, energy conversion, and catalytic reaction in chemical industries. Photocatalytic nanomaterials have emerged as a transformative class of advanced functional materials with significant potential to address global challenges related to environmental pollution, sustainable energy production, and green chemical manufacturing. Various synthesis approaches, such as sol-gel processing, hydrothermal and Solvo-thermal methods, Co-precipitation, Micro-emulsion techniques, chemical vapor deposition, self-assembly, and green synthesis routes, have been developed to produce photocatalytic nanomaterials with controlled morphology, crystallinity, and surface characteristics. Highlighting the unique properties of Nano-materials, such as high surface area, quantum size effects, and tuneable electronic properties, the article emphasizes their effectiveness as photo-catalysts in environmental remediation, energy conversion and wide reaction speed up application in chemical industries. The review discusses the challenges faced in this field as reported on many papers, including limited active sites, charge carrier recombination, and optical absorption, and proposes future research directions to address these gaps. By optimizing band structures, improving charge separation, and exploring novel hybrid materials, the potential of photo-catalytic Nano-materials for solar energy conversion, activation of chemical industry products and environmental remediation can be further enhanced. This article encapsulates the key findings and recommendations of the article papers, offering valuable insights for our researchers those who conduct various applied researches in the field of nanomaterial and photo-catalysis to support our manufacturing industries.

Keywords

Photo-catalytic Nano Materials, Synthesis, Application, Environmental Protection, Energy Conversion, Green Synthesis

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1. Introduction

Rapid industrialization, development of agriculture and urban expansion have significantly increased environmental contamination worldwide, particularly in developing countries such as Ethiopia, where industrial sectors including chemical industries, textiles, tanneries, cement manufacturing, pharmaceuticals, and agro-processing industries are expanding rapidly [1]. They are among the largest consumers of energy worldwide, accounting for a significant share of global electricity and fuel consumption. The growing demand of energy to run these industries again remain major challenges faced by global industrial sectors creating challenges like energy security, environmental protection, and climate change [2]. To address these challenges, industries shall adopt green strategies such as renewable energy utilization, energy-efficient technologies, waste reduction, recycling, and low-carbon manufacturing processes. Although these industries contribute substantially to economic growth and employment opportunities, they simultaneously generate large quantities of hazardous pollutants such as dyes, heavy metals, organic contaminants, toxic sludge, and greenhouse gases [3]. Conventional wastewater treatment technologies often fail to completely remove these contaminants because of high operational costs, poor degradation efficiency, and secondary pollution generation. Consequently, researchers have increasingly focused on photocatalytic nanomaterials as environmentally friendly and energy-efficient alternatives for industrial wastewater treatment and renewable energy applications [4].

Textile factories generate large quantities of colored wastewater containing dyes, surfactants, bleaching agents, suspended solids, and toxic organic compounds [5]. Photo catalytic nanomaterial such as TiO_2, ZnO, and g-C_3N_4 offer effective alternatives for treating textile wastewater because they can generate highly reactive hydroxyl radicals capable of mineralizing organic pollutants into carbon dioxide and water [6]. The leather and tannery industry is another critical sector where photo-catalytic nano-materials could provide substantial environmental benefits [7]. Ethiopia possesses one of Africa's largest leather industries because of its abundant livestock resources. However, tannery industries release wastewater containing chromium compounds, sulfides, dyes, organic matter, and suspended solids [2]. Hexavalent chromium [Cr(VI)] is particularly hazardous because of its carcinogenic and toxic nature. Photo-catalytic Nano-materials such as Fe_3O_4/TiO_2 composites, ZnO nanostructures, and magnetic photocatalysts can facilitate the reduction of Cr(VI) into less toxic Cr(III) while simultaneously degrading organic pollutants.

The cement industry also presents important opportunities for photo-catalytic nanomaterial applications. Cement production is one of the major contributors to carbon dioxide emissions worldwide, including in Ethiopia. Cement emit significant quantities of CO_2, particulate matter, and nitrogen oxides during clinker production and fuel combustion processes. Photocatalytic nanomaterials can contribute to cleaner cement technologies through several approaches. TiO_2-coated cement surfaces possess self-cleaning and air-purification properties because they can degrade atmospheric pollutants such as NOx, volatile organic compounds (VOCs), and airborne organic contaminants under sunlight irradiation [8]. In addition, photocatalytic CO_2 reduction technologies are increasingly investigated for converting carbon dioxide into useful fuels such as methanol and methane using solar energy [9]. Although such systems are still largely at research and pilot scales, future integration into cement industries may contribute to carbon emission mitigation and sustainable industrial production in Ethiopia. Furthermore, photocatalytic coatings on building materials may help reduce urban air pollution and improve infrastructure durability in rapidly growing Ethiopian cities.

Pharmaceutical and chemical industries are also increasingly recognized as important targets for photocatalytic wastewater treatment systems. Pharmaceutical wastewater often contains antibiotics, endocrine-disrupting chemicals, solvents, and biologically active compounds that are difficult to remove through conventional biological treatment methods [10]. Photocatalytic advanced oxidation processes provide efficient degradation pathways for these persistent pollutants. As Ethiopia continues expanding pharmaceutical manufacturing capacity, advanced photocatalytic technologies may become essential for sustainable wastewater management and pollution prevention. Semiconductor nanomaterial such as TiO_2, ZnO, and hetero-junction photocatalysts can effectively degrade pharmaceutical residues under ultraviolet or visible-light irradiation [11].

In the future, Ethiopian chemical industries may also utilize photocatalytic systems for green chemical synthesis, catalytic oxidation reactions, and solar-driven production of valuable chemicals under mild operating conditions [2]. The photo-catalytic field revolves around the utilization of photon energy to initiate various chemical reactions using non-adsorbing substrates, through processes such as single electron transfer, energy transfer, or atom transfer [12]. They emerged as promising catalysts for sustainable chemical industries due to their ability to utilize solar energy for chemical transformations under environmentally benign conditions. Recent studies demonstrate their potential in green chemical synthesis, selective oxidation and reduction reactions, biomass valorization, CO_2 conversion, and renewable fuel production [13]. In particular, photo-catalytic systems facilitate the production of high-value chemicals and pharmaceutical intermediates while reducing energy consumption and hazardous waste generation [14]. Furthermore, advanced photo-catalytic Nano-materials enable the conversion of biomass-derived feed stocks into renewable chemicals and fuels, supporting the transition toward a circular and low-carbon chemical industry.

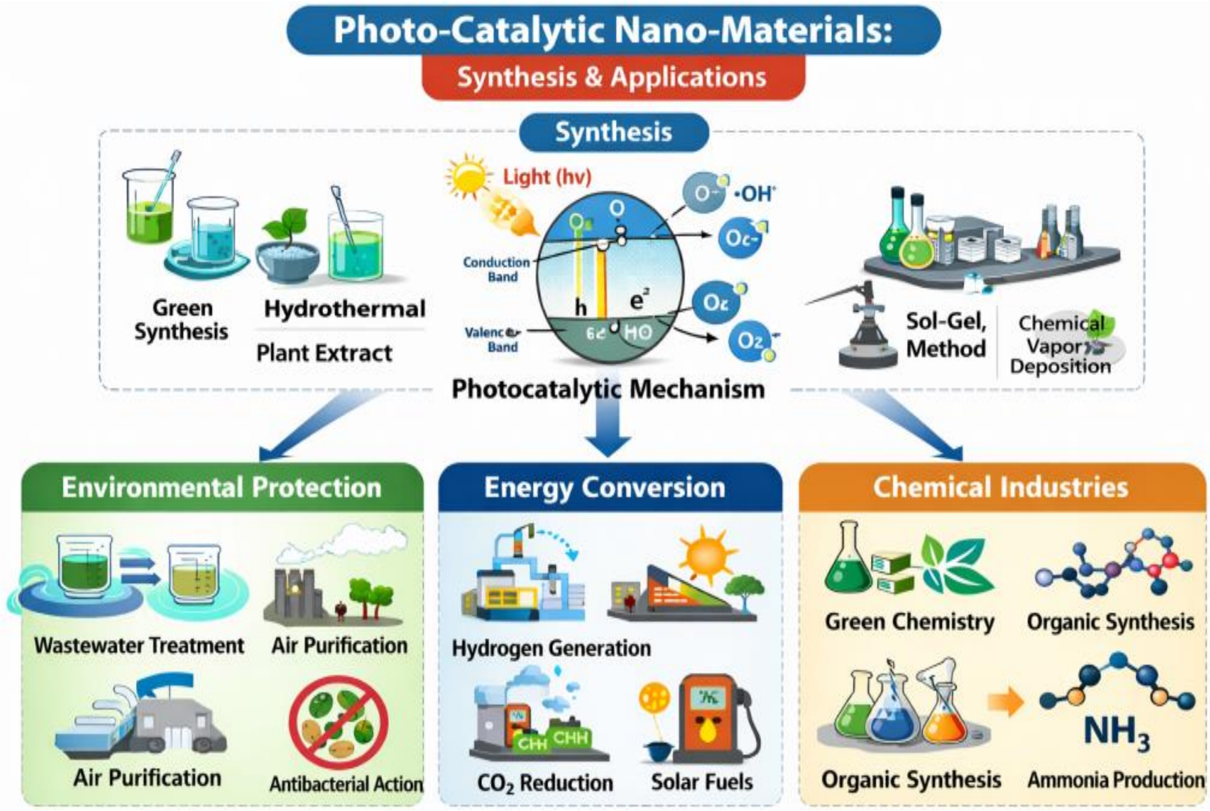

Figure 1. *General representation of photo-catalytic Nano-material synthesis and their application areas.*

Photo-catalytic Nano-materials have emerged as one of the most promising advanced technologies for addressing environmental pollution, proving renewable energy generation, and sustainable chemical production [15]. Nano-materials, particularly those with metallic or semiconducting properties responsive to UV-Vis radiation, have gained popularity due to their unique characteristics compared to larger materials [16]. Finding efficient and stable photo-catalysts is crucial, requiring characteristics like broad light absorption, suitable energy band positions, long charge carrier diffusion paths, and stability [17]. Achieving these qualities in semiconductors is challenging, leading to research on enhancing photo processes through electron structure, surface morphology, and crystal structure modifications. Recent literature explores the synthesis and application of Nano-materials in photo-catalysis [18]. Ideal photo catalysts should possess qualities such as broad light absorption, appropriate energy band positioning, high charge carrier mobility, and stability. Achieving efficient photo processes involves preventing electron-hole pair recombination and facilitating their transport to the semiconductor surface [18]. Enhancing semiconductor efficiency involves modifying electron structure, surface morphology, and crystal structure, as well as broadening radiation absorption through methods like doping and introducing metal nanoparticles [19]. Improving crystallinity and reducing particle size can also minimize recombination centers and enhance charge carrier diffusion which makes it more sustainable for this environmental remediation issues. Tailoring Nano-crystal shapes can enhance selectivity in photo-catalytic processes by enabling selective particle adsorption. The unique properties of Nano-materials, such as high surface area, quantum size effects, and tuneable electronic properties, make them particularly effective as photo-catalysts [20].

Researchers are focusing on factors like band gap, charge carrier behavior, and adsorptive to enhance the performance of these materials. Optimizing band structures and charge separation is crucial for improving hot-carrier generation in photo-catalysts. However, challenges such as low surface area, limited active sites, charge carrier recombination, and optical absorption need to be addressed for commercial applications. On-going research is exploring various aspects of photo-catalytic Nano-materials and their challenges for practical use [20]. In nowadays, on other hand research has been devoted to reducing CO_2 emissions by converting solar energy into chemical energy. Lately, there has been a focus on developing cost-effective technologies to reduce CO_2 emissions by harnessing solar energy for chemical energy conversion [15]. Photo-catalysis has emerged as a promising solution, capable of addressing energy and environmental challenges by utilizing solar energy for various applications such as pollutant degradation, water disinfection, hydrogen production, carbon dioxide reduction, sensing, and therapy [21]. As we can understand from Figure 2 the general illustration of semiconductor photocatalysis process, when a photon is absorbed by the semiconductor, it excites an electron from the valence band to the conduction band, generating a positively charged hole in the valence band. These electron-hole pairs can move to the semiconductor's surface and engage in redox reactions to either degrade or reduce the molecules that are adsorbed.

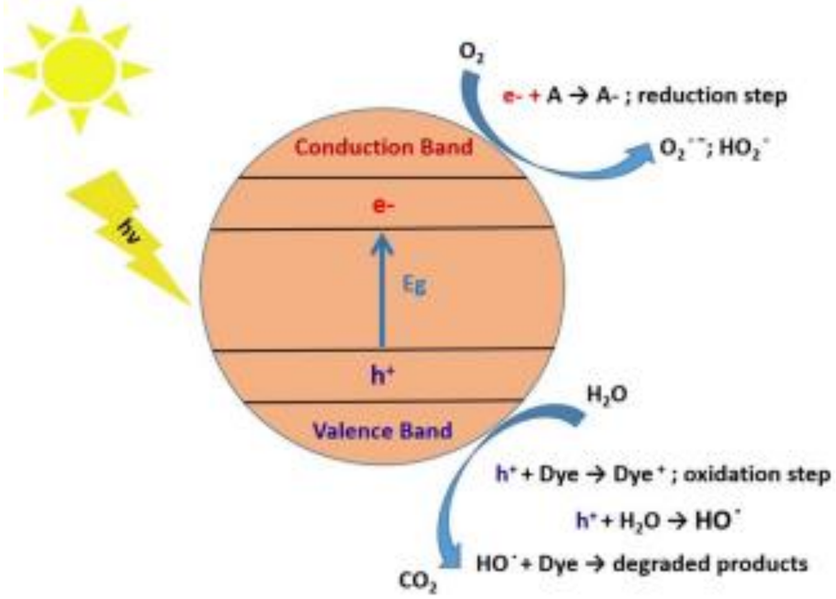

Figure 2. *Illustration of semiconductor photo-catalysis [22].*

$$SC + hv \rightarrow h^{+} + e- \tag{1}$$

$$H_2O + h^{+}\text{ (valance band)} \rightarrow HO^{-} + H^{+} \tag{2}$$

$$h+\text{ (valance band)} + \text{pollutant} \rightarrow \text{Pollutant}^{+} \tag{3}$$

$$HO^{-} + \text{Pollutant} \rightarrow H_2O + CO_2 \tag{4}$$

$$h^{+} + e- \rightarrow \text{Heat} \tag{5}$$

Photo-catalytic materials based on metal oxide Nano-materials like TiO_2, ZnO, CeO, CuO, SnO_2, Bi_2O_3, WO_3, Al_2O_3, NiO, iron-based oxides, among others are leading the way in environmental remediation, particularly in breaking down organic pollutants in wastewater [23]. Hybrid Nano-materials combining semiconductor nanoparticles with materials like carbon Nano-tubes, graphene, or metal nanoparticles show improved photo-catalytic performance and versatility [24]. To the specific, semiconductor quantum dots such as CdS and CdSe offer tuneable bandgaps and high quantum yields, making them promising for solar energy conversion and photo catalysis [25]. Nano-materials, due to their high reactivity and surface-to-volume ratio, are more effective in environmental remediation compared to conventional methods [26]. Metal oxide nanoparticles are particularly studied for photocatalysis as their properties change significantly at the Nano-scale. Nano-materials exhibit superior photo-catalytic performance compared to bulk materials [27].

Photocatalytic nanomaterials are increasingly being utilized in various industries because of their ability to degrade pollutants, purify water and air, generate renewable energy, and support environmentally friendly chemical reactions. In Ethiopia, the application of photocatalytic nanomaterials is still emerging; however, several industrial sectors possess strong potential for adopting these technologies due to increasing environmental pollution, stricter environmental regulations, and growing interest in sustainable industrial development. This review article mainly focus on the recently developed photo catalytic metal oxide Nano-materials, synthesis method and their outstanding performance applications in the areas of environmental remediation, energy conversion and its catalytic activity in chemical industries.

2. Methodology

2.1. Synthesis of Metal Oxide-Based Nano-materials

The synthesis of photo catalytic Nano-materials involves various techniques aimed at producing materials with high surface area, controlled morphology, and enhanced photo catalytic and properties properties.

2.1.1. The Co-precipitation Method

The co-precipitation method is a technique used to prepare metal oxide photo catalysts at ambient temperature. It involves using a precipitating medium and a metal salt precursor to form oxo-hydroxides in water [1]. The commonly used precipitating media in these methods are NaOH, KOH, and $(C_2H_5)_4NOH$, by which it has been established that the morphologies and properties of the metal oxides are highly influenced by the pH of the nature of the alkaline solution. The choice of base and pH level influences the properties of the metal oxides [19].

2.1.2. Micro-emulsion Technique

Microemulsions can be described as a thermodynamically stable system of two immiscible liquids. The dispersed phase, which is present at a lower volume, forms the droplets in a microemulsion [28]. These systems depend on the nature of the dispersed liquid so that dispersion liquids may be classified as either oil in water (O/W), where oil droplets exist dispersed in bulk water, or conversely, water in oil (W/O), where water droplets are dispersed in oil. Stankic et al. introduced the micro-emulsion technique involving two incompatible liquids, oil and water, separated by surfactants. By mixing precise amounts of these components and a metal oxide precursor through continuous stirring, a homogenized phase is achieved [29]. Nanoparticles are formed by adding precipitating agents and centrifuging the mixture. The resulting nanoparticles are then washed and dried. Micro-emulsions serve as Nano-reactors for Nano-particle creation, with the advantage of controlling size and shape [30]. However, the method requires multiple washing steps and may lead to Nano-particle aggregation, necessitating stabilizers [31].

2.1.3. Hydrothermal Synthesis

This manufacturing process also known as Solvo-thermal, involves using water as a solvent. In this process, metal complexes are thermally decomposed by boiling them in an inactive atmosphere or in an autoclave [29]. To prevent agglomeration of particles, a capping agent or stabilizer is added at the right time during the reaction. These stabilizers not only hinder particle growth but also aid in dissolving the particles in various solvents.

2.1.4. Green Synthesis

Conventional laboratory methods for Nano particle fabrication have drawbacks like bioaccumulation, human error, instability, and difficulty in recycling [32]. To overcome these issues, a new approach called green synthesis is gaining popularity. This method focuses on using sustainable and environmentally friendly techniques to prevent the formation of harmful by-products. These are achieved in two necessary fabrication mechanism: namely Biological component for green synthesis and solvent system based green synthesis.

Biological Components for Green Synthesis

Green synthesis of nanoparticles utilizes biological agents such as bacteria, fungi, and plant extracts is an environmentally friendly method that requires low energy activation for reactions [33]. Bacteria are effective in reducing metal ions, while fungi have intracellular enzymes and proteins that aid in Nano-particle synthesis [34]. Plant extracts, rich in biomolecules, are also used for Nano-particle preparation. Although biological synthesis has limitations in controlling size and yield, and can be slow, it remains a promising method for Nano-particle production [35].

Solvent System-Based Green Synthesis

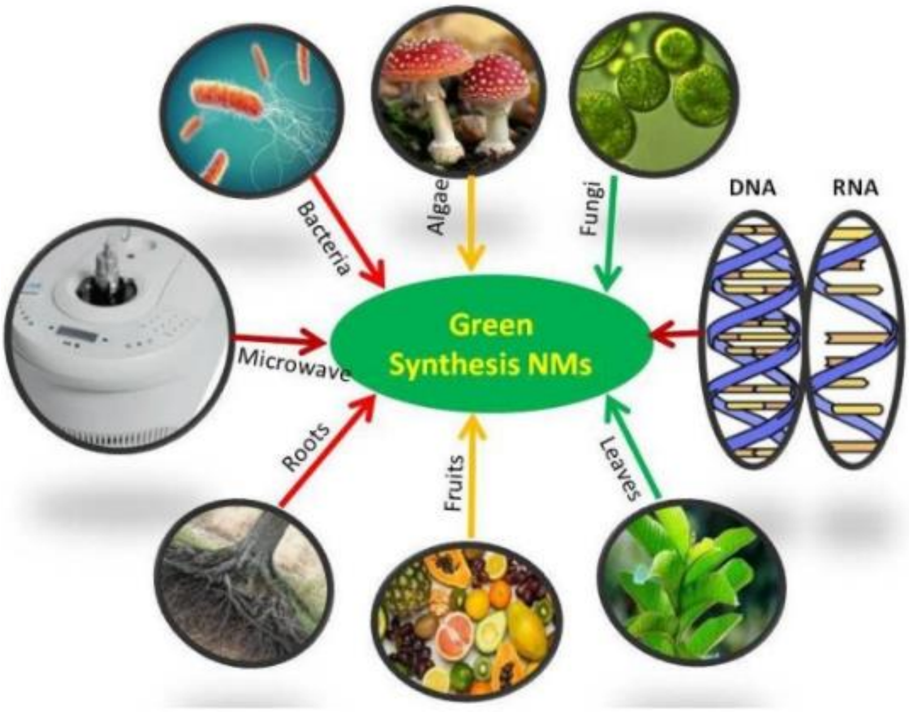

Figure 3. *Green synthesis of photo-catalysts [36].*

Solvent systems play a crucial role in the synthesis process, whether it is a "green" procedure or not. While water is the most preferred solvent, there are limitations to its use in certain cases. New trends in ionic and supercritical liquids have emerged to address issues related to toxic and non-toxic solvents in Nano-particle production and renewable sources. Ionic liquids have the advantage of readily dissolving numerous materials, offering a wide temperature range during operation, and being non-coordinating against polarity. They also have no vapor pressure, making evaporation into the environment a non-issue. Supercritical fluids, on the other hand, are created by subjecting ordinary solvents to extreme temperatures and pressures, altering their properties significantly to overcome the limitations of conventional liquids.

2.1.5. Self-Assembly

Self- Assembly techniques mimic natural self-assembly processes, such as block copolymer self-assembly, to create periodic nanostructures through phase separation. This method results in ordered structures with various shapes [37]. Another approach involves evaporating nanoparticles onto a liquid-air interface, leading to the formation of Nano-particle islands and subsequent monolayer growth. Liquid crystals can also be used for self-organization to create three-dimensional synthetic materials with strong resonances in the visible spectrum [38].

2.1.6. Gas-Phase Deposition Techniques

Gas-phase deposition includes two main methods: Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) [39]. Physical Vapor Deposition (PVD), known for its eco-friendly approach, involves vaporizing the material and condensing it onto a surface, suitable for coating flat or simple shapes. On the other hand, Chemical Vapor Deposition (CVD) introduces gas substrates into a chamber to form coatings through chemical reactions, allowing for coating three-dimensional parts [40]. Plasmonic materials like silver and gold are commonly used, with silver offering low losses for visible and near-infrared light, while gold provides higher chemical stability. Alternative plasmonic materials include nitrides, doped transparent conducting oxides, graphene, and metals like copper, aluminum, chromium, or iridium [41].

2.1.7. Sol-Gel Process

The Synthesis, Properties, and Applications of Oxide Nanomaterials discuss the sol-gel process used to prepare metal oxides by hydrolyzing metal reactive precursors in an alcoholic solution. This results in the formation of a metal hydroxide polymer that condenses into a densely packed porous gel. Heating and drying the gel produces a metal oxide powder crystal of the desired particle size. The resulting metal oxide can be in the form of nanoparticles, bulk material, or oxygen-deficient based on the heat treatment. For example, copper oxide nanoparticles were produced using copper (II) acetate in ethanol as a precursor in this method [42].

2.2. Photo-catalysis Operating Parameters

Various external factors, known as operating or extrinsic parameters, can influence the rate of a photo-catalytic reaction [41]. These factors include the catalyst concentration, temperature, pH of the solution, initial concentration of the organic compound and oxygen content.

2.2.1. Concentration of the Catalyst

Research has indicated that the concentration of the catalyst is directly related to the number of electron-hole pairs produced. Increasing the catalyst amount enhances the active sites on the photo catalyst surface, leading to a higher rate of the photoreaction. However, the reaction rate peaks at a certain concentration level, known as the limit concentration, where total absorption occurs. Beyond this limit, the photoreaction rate may decline [40].

2.2.2. Temperature

Prior research has demonstrated that photo-catalytic systems can operate without the need for additional heat as they are triggered by photons. Photo reactions are generally unaffected by minor temperature changes. Lower temperatures enhance adsorption, a naturally exothermic process. However, temperatures exceeding 80 ℃ can impede the exothermic adsorption of pollutants. Experiments utilizing high-power lamps for photo-catalysis are typically outfitted with cooling mechanisms to sustain a system temperature of 25 ℃ [39].

2.2.3. PH Value

Researchers have found that the pH level impacts the charged surfaces of semiconductors and pollutants, affecting particle size in water and pollutant adsorption on semiconductor surfaces. Studies show that lower pH levels lead to higher degradation rates of pollutants during photo catalytic processes [39].

2.2.4. Initial Concentration of Pollutant

Several studies have found that the photo catalytic activity of catalysts decreases when the initial concentration of pollutants is high, while the photo degradation of pollutants increases at lower concentrations [39].

2.2.5. Oxygen Content in the Medium

Huang conducted a study on the impact of adding H_2O_2 to the process of decolorizing methyl orange. They found that the rate of decolorization increased as the concentration of H_2O_2 increased, with an optimal concentration of 1.2 mmol L for the photo catalytic decolorization of methyl orange solution using Pt.-modified TiO_2 [39]. In photocatalytic nano-materials synthesis, the oxygen content in the reaction medium was observed as very detrimental factor to decide the best reaction condition.

2.3. Mechanisms of Photo Catalysis

The band gap is the energy difference between the valence band and conduction band of a semiconductor. Photo catalyst semiconductors like TiO_2, ZnO, ZrO_2, and CdSe absorb ultraviolet energy from sunlight or artificial light sources to create electron-hole pairs only if the energy exceeds the band gap. When illuminated, the conduction band electron of the photo catalyst becomes excited, entering a photo-excitation state. The electron is negative and the hole is positively charged. The positively charged hole in the valence band splits water molecules into hydrogen gas and high-energy hydroxyl free radicals. The electron reacts with oxygen to produce superoxide anions. This cycle continues as long as light energy is present. The process of photo catalysis involves chemical reactions explained through equations i-ix below [39]. When semiconductor photo catalysts are exposed to light, valence band electrons move to the conduction band, creating positively charged holes. For enhanced efficiency, it is crucial that these electrons and holes spend more time before recombining. The resulting reactive species like OH• radicals help reduce recombination rates and interact with organic pollutants. The energy requirements for wastewater treatment suggest that the CB of the photo catalyst must be more negative than the reduction potential of $H+/H_2$, while the VB must be more positive than the oxidation potential of H_2O/O_2. Visible light, with energy greater than 1.23 eV, can drive photo catalysis for wastewater treatment.

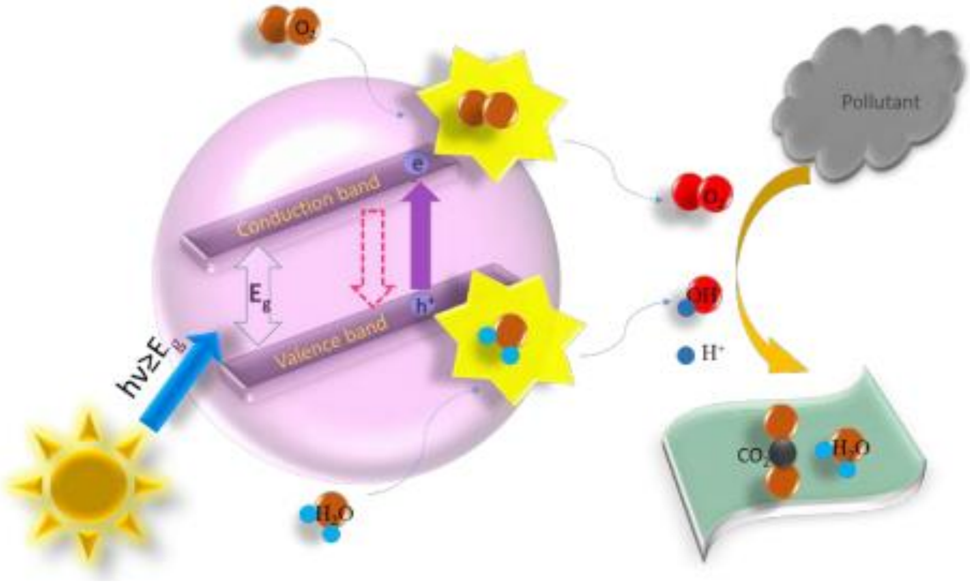

Figure 4. *The Degradation of pollutant by heterogeneous photo catalysis.*

Here, the redox potentials (E0) of some active radicals, such as $H+ /H_2$, O_2 / O_2- and H_2O/OH should be noted as 0V, -0.33 V and -0.42 V, respectively.

The photo-catalytic oxidation of organic compounds under UV light can be presented as follows:

$$\text{Semiconductor photo-catalyst} + hv \rightarrow e\text{-}_{CB} + h^{+}_{VB} \tag{6}$$

$$h^{+} + H_2O \rightarrow H^{+} + OH^{*} \tag{7}$$

$$h^{+} + OH^{-} \rightarrow OH^{*} \tag{8}$$

$$e^{-} + O_2 \rightarrow O_2^{-} \tag{9}$$

$$2e^{-} + O_2 + 2H^{+} \rightarrow H_2O_2 \tag{10}$$

$$e^{-} + H_2O_2 \rightarrow OH^{*} + OH^{-} \tag{11}$$

$$\text{Organic pollutant} + OH^{*} \rightarrow \text{degradation product} \tag{12}$$

$$\text{Organic pollutant} + \text{semiconductor photo-catalyst } (h+VB) \rightarrow \text{oxidation products} \tag{13}$$

$$\text{Organic pollutant} + \text{semiconductor photo-catalyst } (e\text{-}CB) \rightarrow \text{reduction products} \tag{14}$$

When an excited electron-hole pair recombines, it releases excess energy in the form of heat, which is not ideal for efficient photo catalysis. The main goal of photo catalysis is to facilitate a catalytic reaction between the excited electrons and oxidants to produce a reduced product. Additionally, a reaction between the generated electrons and a reductant is necessary to yield an oxidized product. These reduction and oxidation reactions take place on the surface of photo catalysts, creating positive holes and electrons. In the oxidative reaction, positive holes interact with moisture on the catalyst surface to produce hydroxyl free radicals. Introducing more oxygen from outside the photo-catalytic reactor can act as electron acceptors and enhance pollutant degradation by slowing down recombination. The time required for complete pollutant degradation increases as the amount of photo-catalyst decreases.

2.3.1. Heterogeneous Photo Catalysis

Heterogeneous photo catalysis is a well-established field within chemical catalysis known for its applications in wastewater treatment and air purification. Unlike homogeneous catalysis, the catalyst in this process is in a different phase from the reactants [43]. Various reactions can be achieved through heterogeneous photo catalysis, including dehydrogenation, oxidations, hydrogen transfer, water detoxification, metal deposition, isotopic exchange, and pollutant removal. Transition metal oxides and semiconductors are commonly used as heterogeneous photo catalysts due to their exceptional properties.

2.3.2. Homogeneous Photo Catalysis

In a homogeneous photo catalytic reaction, both the reactants and photo catalysts are in the same phase [44]. The homogeneous photo catalysts include ozonolysis and photo-Fenton systems. Fenton discovered that combining hydrogen peroxide and Fe(II) in an acidic environment creates strong oxidizing properties. The mechanism of this Fenton reaction, known for producing hydroxyl radicals, is still debated. It involves a redox reaction where Fe(II) is oxidized to Fe(III) by H_2O_2, leading to the formation of hydroxide ions and hydroxyl radicals.

The hydroxyl radical production mechanism of by ozone can occur in the following paths.

$$O_3 + hv \rightarrow O_2 + [O] \tag{15}$$

$$[O] + H_2O \rightarrow H_2O_2 \tag{16}$$

$$H_2O_2 + hv \rightarrow {}^*OH + {}^*OH \tag{17}$$

$$[O] + H_2O \rightarrow {}^*OH + {}^*OH \tag{18}$$

In the same way, the Fenton system yields hydroxyl radicals by the following:

$$Fe^{+2} + H_2O_2 \rightarrow {}^*OH + Fe^{3+} + OH^- \tag{19}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{+2} + {}^*OOH + H^+ \tag{20}$$

$$Fe^{+2} + {}^*OH \rightarrow Fe^{3+} + OH^- \tag{21}$$

In a photo Fenton kind reaction process additional source of *OH generated over photo catalysis of hydrogen peroxide and reduction of Fe^{3+} ions in the presence of light energy.

$$H_2O_2 + hv \rightarrow 2OH\ {}^* \tag{22}$$

$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{+2} + H^+ + {}^*OH \tag{23}$$

The effectiveness of photon-Fenton processes depends on factors like pH, H_2O_2 concentration, and UV light intensity. One advantage is that it can utilize solar energy up to 470 nm without needing expensive UV or electrical sources. Photon-Fenton reactions are considered more efficient than other photo catalytic reactions. However, a drawback is the need for low pH levels due to iron precipitation at higher PH [45].

2.4. Applications of Photo Catalytic Nanomaterials

Photocatalytic nanomaterials have emerged as versatile materials for addressing environmental, energy, and industrial challenges due to their ability to utilize solar energy for chemical transformations. Their ability to harness solar energy for pollutant degradation and chemical conversion makes them key materials for future green technologies. Also their unique physicochemical properties, including high surface area, tunable band gaps, and enhanced charge separation, enable efficient degradation of pollutants and conversion of solar energy into valuable products [46]. Metal oxide nanostructures have distinct physical and chemical properties that make them valuable for various applications. These include removing heavy metals, detecting poisonous gases, coating textiles for wearable electronics, biomedical uses, and degrading organic contaminants through photo catalysis.

2.4.1. Photo Catalytic Removal of Organic Pollutants

Photocatalytic degradation is a highly efficient technique for eliminating organic pollutants such as antibiotics, organic dyes, toluene, nitrobenzene, cyclohexane, and refinery oil from the environment [47]. Transition metal oxides and their composites have shown great potential in photo catalytic activities for breaking down organic contaminants [48]. They have controlled structures and surfaces, acting as semiconductors with wide band gaps and are non-toxic and stable in water, making them effective for degrading organic pollutants through photo catalysis.

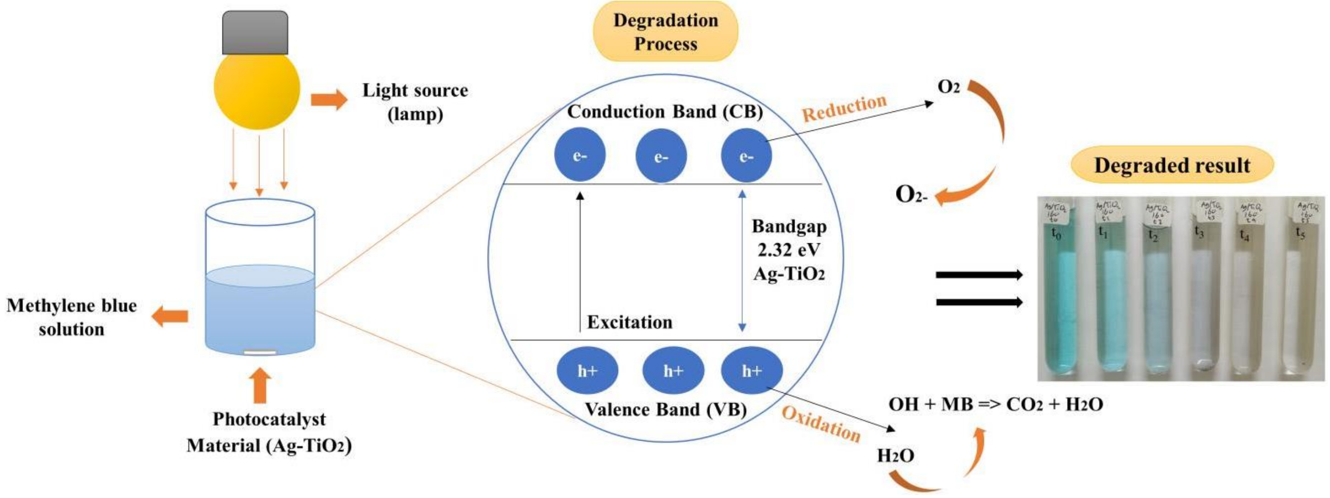

Figure 5. *Environmental application of Photo-catalytic Nano-materials.*

2.4.2. Energy Conversion and Storage

Researchers are working on finding renewable energy sources and reducing the carbon footprint to address the world's energy and environmental crisis. Various energy storage systems, including transition metal oxides, have been developed to tackle these issues. Semiconductor metal oxides like TiO_2, ZnO, WO_3, $BiVO_4$, and Fe_2O_3 are effective in photo electrochemical water splitting for producing clean hydrogen fuel using solar energy [49]. Metal oxide Nano-particle photo electrodes show better performance due to their large surface areas and shorter diffusion distances. Metal oxides are also used in solar cells, fuel cells, and energy storage devices like lithium-ion batteries and super capacitors [50]. Their morphology can be engineered to achieve high power density for fast charging, making them valuable for electrochemical energy conversion, storage, and catalysis applications.

2.3.3. Poisonous Gas Sensing (Sensor for E-Nose Technology)

Metal oxide semiconductors like SnO_2, In_2O_3, Fe_2O_3, WO_3, and Cr_2O_3 have been used for gas sensing, particularly for monitoring toxic gases like ammonia due to its potential health hazards [51]. Various regulations limit the concentration of ammonia in different settings. NiO-based sensors have shown promise in detecting ammonia, with recent advancements in using a TiO_2/NiO bilayer sensor for improved performance at lower temperatures. Additionally, metal oxide-based gas sensors are utilized in e-nose technology for on-site monitoring of odours, with Figaro type sensors proving to be the most suitable for long-term applications [52]. The use of univariate multiplicative factors has been effective in addressing sensor drift in real-time odour measurements.

2.3.4. Photo-catalytic Reduction of CO_2

Nowadays the rise in fossil fuel consumption has led to increased CO_2 levels in the atmosphere, causing environmental pollution and an energy crisis. To combat this, researchers are focusing on photo-catalytic reduction of CO_2 into energy fuels like methane and methanol [50]. Titanium dioxide is a key photo-catalyst for this process. Recent studies have shown that carbon Nano-fibers-supported TiO_2 Nano-crystals with specific facets exhibit enhanced performance in CO_2 reduction [53]. Additionally, modifying TiO_2 with Ag noble metal and activated carbon improves its efficiency in CO_2 photo-reduction, increasing the CO conversion rate significantly.

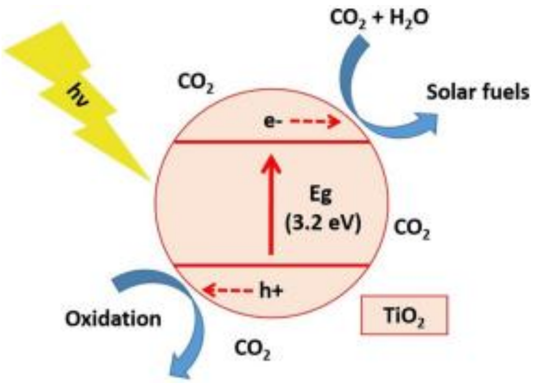

Figure 6. *Schematic illustration of the mechanism for the photo-catalytic reduction CO_2 on the TiO_2.*

2.3.5. Hydrogen Generation

Hydrogen production through photo-catalysis involves decomposing organic species like alcohols and acids, with the main goal being to use water or polluted effluents as a direct source of hydrogen [54]. There are three mechanisms used for hydrogen production: dehydrogenation of alcohols, water splitting, and alcohol reforming. Various photo-catalysts like TiO_2, $SrTiO_3$, $KTaO_3$, and CdS are used for these processes [55]. The hydrogen produced is not pure and is accompanied by other species like CO_2, alkanes, and aldehydes. Researchers have studied different catalysts like $AuAg/TiO_2$ for efficient hydrogen production, showing that the metal loading and preparation method are crucial factors.

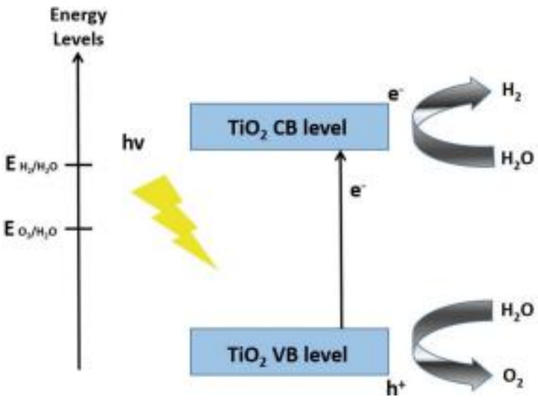

***Figure 7**. The photo-catalytic production of hydrogen by TiO_2.*

3. Conclusion and Recommendation

In conclusion, as a general this review paper underscores the remarkable progress in the synthesis and application of photo-catalytic Nano-materials while also shedding light on existing gaps in the research area. Despite the advancements made in enhancing semiconductor efficiency and radiation absorption in Nano-materials, the remaining challenges such as limited active sites, charge carrier recombination and optical absorption need to be addressed for practical applications. Future work in this field should focus on overcoming these challenges by optimizing band structures, improving charge separation, and developing visible light responsive photo-catalysts for more efficient solar energy conversion, environmental remediation and activating chemical reaction of chemical industries. Additionally, exploring novel hybrid materials, such as carbon Nano-tubes, graphene, and metal nanoparticles, and investigating semiconductor quantum dots with tuneable band-gaps can further enhance the performance and versatility of photo-catalytic Nano-materials. By addressing these gaps and pursuing innovative research directions, the potential for utilizing photo-catalytic Nano-materials in environmental protection, energy conversion, and green chemical reactions can be maximized for a sustainable future.

Regarding our country, most existing studies remain limited to laboratory-scale investigations, while pilot-scale implementation and industrial integration are still underdeveloped. High synthesis costs, insufficient research infrastructure, limited technical expertise, and weak collaboration between industries and universities hinder commercialization of these technologies. Nevertheless, increasing environmental awareness, stronger governmental regulations, and expanding renewable energy initiatives may accelerate future adoption of photo-catalytic systems in Ethiopian industries. Future research should therefore focus on developing low-cost visible-light-responsive photo-catalysts, magnetic recoverable nanocomposites, solar-driven photo-catalytic reactors, and industrial pilot-scale systems adapted to local Ethiopian conditions and industrial wastewater characteristics.

Abbreviations

CB	Conduction Band
CVD	Chemical Vapor Deposition
POPs	Persistent Organic Pollutants
PVD	Physical Vapor Deposition
VB	Valance Band

Author Contributions

Lamessa Abdisa: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigations, Methodology, project administrations, Resources, Software, Supervision, Validations, Visualizations, Writing – original draft, Writing – review & editing

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Conflicts of Interest

The author declare that there is no conflict of interest regarding this review article.

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