

Article

Photocatalytic Applications of Metal Oxides for Sustainable Environmental Remediation

Mir Sayed Shah Danish ^{1,2,*}, Liezel L. Estrella ³, Ivy Michelle A. Alemaida ⁴, Anton Lisin ⁵, Nikita Moiseev ⁶, Mikael Ahmadi ⁷, Massoma Nazari ⁸, Mohebullah Wali ⁹, Hameedullah Zaheb ² and Tomonobu Senjyu ⁷

¹ Strategic Research Project Center, University of the Ryukyus, 1 Senbaru 9030213, Japan

² Department of Energy Engineering, Kabul University, Jamal Mina 1006, Afghanistan; hameedzaheb@gmail.com

³ Department of Chemistry, Silliman University, Hibbard Avenue, Dumaguete City 6200, Negros Oriental, Philippines; liezellestrella@su.edu.ph

⁴ Department of Chemistry, University of San Carlos—Talamban Campus, Talamban, Cebu City 6000, Philippines; usc.alemaidaim@gmail.com

⁵ Financial Faculty, Financial University under the Government of the Russia Federation, 125993 Moscow, Russia; avlisin@fa.ru

⁶ Department of Mathematical Methods in Economics, Plekhanov Russia University of Economics, 117997 Moscow, Russia; moiseev7877@ya.ru

⁷ Department of Electrical and Electronics Engineering, University of the Ryukyus, 1 Senbaru 9030213, Japan; ahmadi.micaeil@gmail.com (M.A.); b985542@tec.u-ryukyu.ac.jp (T.S.)

⁸ Infrastructure Project Management Team (IPMT), Pacific Architects and Engineers (PAE)-CSSP, Zohak Village, Kabul, Afghanistan 1002, Afghanistan; masooma.nazari@pae.com

⁹ Department of Electrical and Electronics Engineering, Kabul University, Jamal Mina 1006, Afghanistan; m.wali@ku.edu.af

* Correspondence: mdanish@lab.u-ryukyu.ac.jp



Citation: Danish, M.S.S.; Estrella, L.L.; Alemaida, I.M.A.; Lisin, A.; Moiseev, N.; Ahmadi, M.; Nazari, M.; Wali, M.; Zaheb, H.; Senjyu, T. Photocatalytic Applications of Metal Oxides for Sustainable Environmental Remediation. *Metals* **2021**, *11*, 80. <https://doi.org/10.3390/met11010080>

Received: 13 December 2020

Accepted: 28 December 2020

Published: 2 January 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: Along with industrialization and rapid urbanization, environmental remediation is globally a perpetual concept to deliver a sustainable environment. Various organic and inorganic wastes from industries and domestic homes are released into water systems. These wastes carry contaminants with detrimental effects on the environment. Consequently, there is an urgent need for an appropriate wastewater treatment technology for the effective decontamination of our water systems. One promising approach is employing nanoparticles of metal oxides as photocatalysts for the degradation of these water pollutants. Transition metal oxides and their composites exhibit excellent photocatalytic activities and along show favorable characteristics like non-toxicity and stability that also make them useful in a wide range of applications. This study discusses some characteristics of metal oxides and briefly outlined their various applications. It focuses on the metal oxides TiO₂, ZnO, WO₃, CuO, and Cu₂O, which are the most common and recognized to be cost-effective, stable, efficient, and most of all, environmentally friendly for a sustainable approach for environmental remediation. Meanwhile, this study highlights the photocatalytic activities of these metal oxides, recent developments, challenges, and modifications made on these metal oxides to overcome their limitations and maximize their performance in the photodegradation of pollutants.

Keywords: photocatalyst; metal oxide; organic pollutant; photocatalytic degradation

1. Introduction

Environmental contamination has been observed along with the global rise in the number of various industries together with rapid urbanization. As a consequence, various toxic organic pollutants as well as several microorganisms that may even be pathogenic are released into the environment. One of the biggest challenges worldwide now is finding means to provide sustainable living conditions for future generations. To address this, environmental remediation is now required and its study is highly advocated. Environmental remediation refers to the reduction/removal of pollutants or contaminants from

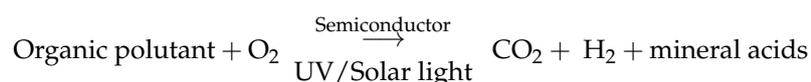
air, water and soil for the protection of living systems and the environment against further deterioration [1]. Wastewater treatment facilities have been employed for environmental remediation as a way to restore water that has been used and/or contaminated back to a desirable quality [2].

Pollutants released into the environment can be classified into four categories: chemical, physical, physiological, and biological. Chemical pollutants can be broadly categorized into inorganic and organic pollutants, where organic pollutants may be defined as those compounds containing organic carbon [2]. Oil, synthetic organic materials, and oxygen demanding wastes are those that are considered organic pollutants. Oxygen demanding wastes include effluent from municipal and domestic, food and canning industries, paper and pulp mills, distilleries and they compete with aerobic species in the aquatic environment thereby heavily affecting the aquatic life [3]. Furthermore, pharmaceuticals, food additives, detergents, plastics, pesticides, solvents, paints, fibers, and volatile organic compounds (VOCs) are those that are considered synthetic organic pollutants. These pollutants go into the environment from their manufacture to their use in different applications and even spillage during transport [4].

As a consequence of the harmful effects mentioned above, most research works currently focus on organic pollutants. Dyes are another class of organic pollutants causing notable environmental pollution released by many industries, with an estimation of more than 7×10^5 tons of dyes produced per year and roughly 10% of this is released to the environment [5]. These dyes prevent the reoxygenation capacity of water bodies which results in stoppage of most biological activity in aquatic life. Dyes also cut off sunlight, preventing the photosynthesis process of aquatic plants or algae [6]. Azo dyes are the most common constituting 60–70% of textile dyes. Most of the azo dyes have >2000 h of half-life under the sunlight. Consequently, efficient and fast degradation of these dyes is very challenging and crucial for water remediation [7]. Furthermore, azo dyes were identified as potential carcinogens. Adsorption of these dyes through the gastrointestinal tract, skin, or lungs has been found to cause serious health problems, including the formation of hemoglobin adducts and disruption of blood formation. Many azo dyes are found to cause DNA damage leading to the formation of malignant tumors [8]. Effluents from chemical, ink, textile, metallurgical and mining industries, among others, therefore contain carcinogenic and mutagenic dyes and are released into aquatic systems and may seep into our ground waters [9]. Noting that these compounds have harmful effects to human and aquatic life, there is a worldwide sense of urgency in addressing these concerns. The textile industry is the greatest contributor to dye pollution.

Some approaches to decontaminate water include adsorption, membrane filtration, biological degradation, photocatalytic degradation, liquid-liquid extraction, nanofiltrations, oxidation, reverse osmosis, UV irradiation among others [7]. This review article focuses on photocatalytic degradation approach. Consequently, various materials have been utilized according to the type of wastewater treatment technology and among these is the use of a photocatalyst to degrade water pollutants [10].

Photocatalysis, from its name, involves photons and a catalyst and is fundamentally a process that involves the absorption of light by a catalyst to initiate and hasten chemical reactions leading to the mineralization of the pollutants. It has the overall equation [9,11]:



Photocatalysis presents a lot of advantages over other conventional catalytic techniques. Firstly, reaction conditions such as sunlight, room temperature, and normal atmospheric pressure are common and are readily available. Second, the degradation process is pollution free producing no harmful products and by-products. From the fact that the core of photocatalytic technology is a photocatalyst, and a lot of materials can act as a photocatalyst, therefore, it becomes a flexible, comprehensible and economic-friendly technology

in waste water treatment processes for the removal of the harmful contaminants without causing secondary pollution to provide a sustainable environment [10,12,13].

Advanced oxidation processes (AOPs) are employed now that pollution has increased considerably for the reason that self-purification by simple aerial oxidation is no longer sufficient to address the pollution. AOPs make use of highly reactive oxidative radicals, such as hydroxyl radicals and then the reaction of these radicals to the pollutants. AOPs include semiconductor photocatalysis, Fenton, photo-Fenton, UV/H₂O₂, ozonation, and O₃/H₂O₂ processes. Among the AOPs, we focus on photocatalysis. Semiconductor photocatalysis has been recognized as one of the green methods of addressing global energy and environmental difficulties from its effective use of the naturally occurring and inexhaustible solar energy which makes it an ideal choice for the removal of organic contaminants from wastewater [11].

As stated earlier, photocatalysis involves photons and a catalyst. A catalyst material is a material that is neither changed nor consumed during chemical reactions. A semiconductor metal oxide is employed as a photocatalyst that generates a redox reaction at its surface when activated by UV-visible light appropriate to its band gap [10]. This is the fundamental mechanism of photocatalytic degradation of organic contaminants—driven by the oxygen on the surface of the semiconducting photocatalyst. The energy of photon absorption of the semiconducting metal oxide activates the oxygen then converts the organic pollutants into less toxic products/intermediates [7]. A more detailed discussion of the mechanism of photocatalysis is given below under the photocatalytic applications of metal oxides.

Fujishima and Honda's pioneering 1972 research on the splitting of water into H₂ and O₂ by means of photocatalysis producing hydrogen gas available for fuel shifted the focus of research onto heterogeneous photocatalysis for environmental remediation [14]. In heterogeneous photocatalysis, the photocatalytic reactions occur either at the interface between the solid semiconductor and the gaseous or liquid medium. This a good approach for degradation of pollutants in air and water [15].

The main disadvantage of a photocatalytic process is that the metal oxide semiconductors only use of a small range of the solar spectrum, i.e., UV light which is only 5% of the solar spectrum. Modifications by engineering of the metal oxides via chemical and structural changes to widen band gaps, doping of hetero-atoms, and preparation of nanocomposites is done to address this concern. Good photocatalysts will now be able to absorb including the visible range of the solar spectrum efficiently, suspend or delay the recombination of holes and electron pairs, to efficiently perform as photocatalysts [7].

Metal oxide-based heterostructures, a closely packed structure formed when metal ions form coordination bonds with oxides, show promising wide range applications because of their distinctive physical and chemical properties [10]. Metal oxides have been highly studied in understanding physical (i.e., electron transport, transparency and magnetism) and chemical (i.e., gas sensing, photocatalysis) phenomena because their characteristics of having strong electron-electron interaction in addition to their compositional simplicity and stoichiometric diversity [16]. In addition, modification of the metal oxides can be made by chemical and structural changes, doping of hetero-atoms, or preparation of nanocomposites which makes them more interesting and thus highly studied [7]. Furthermore, they are noted to have remarkable recycling rate and good stability making them efficient for various applications [13]. Hence, metal oxides have been used in a variety of applications such as removal of heavy metals, poisonous gas sensing, textile coating for wearable electronic devices, biomedical applications, and photocatalytic degradation of organic contaminants.

The transition metal oxides and their composites exhibit excellent photocatalytic reactions for the degradation of organic contaminants. Metal oxide-based nanomaterials with well-controlled structural, crystalline, and surface features function as semiconductors with wide band gaps. They also show favorable characteristics like non-toxicity and high stability in the water [7]. Photocatalytic materials should be more abundant on Earth, cost-effective, and non-toxic for sustainability in various energy and environmental fields

and employing metal oxides as catalysts suit well into these characteristics [13]. TiO₂ and ZnO are two examples of metal oxides close to being called ideal photocatalysts due to their excellent photocatalytic properties [10]. They will be discussed later in more detail.

Recent developments in nanotechnology have paved innovative ways for environmental remediation, especially in wastewater treatment, wherein nanomaterials are employed in water purification through mechanisms such as the adsorption of pollutants and heavy metals, the degradation of toxic materials into less harmful compounds by catalysis, and the deactivation of pathogens [11]. Jeevanandam et al. [17] described nanomaterials as materials with length of 1–1000 nm in at least one dimension; however, they are commonly defined to be of diameter in the range of 1 to 100 nm in principle. Nonetheless, there is no single definition of a nanomaterial that is accepted internationally and the definition changes for every organization. For example, nanomaterials are described as a material with any external nanoscale dimension or having internal nanoscale surface structure by the International Organization for Standardization (ISO) while the European Union (EU) Commission has described nanomaterials as a manmade or natural-occurring material whose particles are either unbound, aggregated or agglomerated having an external dimension which ranges between 1–100 nm size [17].

Despite the chemical and biological side effects of nanosized metal oxides, they have been highly used for environmental remediation [1]. Nanomaterials can come in various shapes/morphologies, such as nanoparticles, tubes, wires, and fibers, and can function as absorbents and catalysts. The detection and removal of gases (SO^{−2}, CO, NO_x, etc.), contaminated chemicals (arsenic, iron, manganese, nitrate, heavy metals, etc.), organic pollutants (aliphatic and aromatic hydrocarbons) and biological substances (viruses, bacteria, parasites and antibiotics) are also done by nanomaterial composites with polymers [18].

The nanoparticles of transition metal oxides are used for adsorption processes due to the fact that they exhibit remarkable surface characteristics, microstructural features, and high surface area. The active sites and high surface area enable effective adsorption events. Surface-to-volume ratio is increased when materials are brought down to size from bulk to the nanoscale. The surface energy of adsorbent materials is increased by reducing the size and more active sites on their surface are available for organic molecules to interact. Thus, nanomaterials show better adsorption capacity compared to the bulkier counterparts [7].

In general, because of their surface-to-volume ratio and their associated intrinsic high reactivity, nanomaterials show better performance in environmental remediation than other conventional techniques [18]. Consequently, nanoparticles of metal oxides are extensively studied for photocatalysis. This is because of the property of the materials that change radically when the size of the materials reaches to nanoscale range. The exploitation of nanomaterials thus displays higher photocatalytic performance than their bulk counterparts [13]. The commonly used nanosized metal oxides in the field of environmental remediation include TiO₂, ZnO, CeO, CuO, SnO₂, Bi₂O₃, WO₃, Al₂O₃, NiO, iron-based oxides, and others [1].

This review article discusses the outstanding performance and recent developments of metal oxide nanomaterials focusing on the photocatalytic applications on some of the most common metal oxide nanostructured photocatalysts namely TiO₂, ZnO, CuO, Cu₂O and WO₃. These metal oxides are known to be cost-effective, stable, efficient and environment-friendly materials for environmental remediation [13].

2. Metal Oxides-Based Nanomaterials

2.1. Characteristics and Properties

In recent decades, metal oxides have played a lead role in the fields of physics, chemistry and material science. Particularly because of the unique physical and chemical properties of metal oxide nanostructures that leads to wide scope of applications some of which are the removal of heavy metals, poisonous gas sensing, textile coating for wearable electronic devices, biomedical applications, and photocatalytic degradation of organic contaminants, among others [10,18].

Discussing the effect of bringing down to nanoscale, when the particle size is small, a bigger fraction of atoms would be on the surface of nanoparticles. The increased surface area in nanostructured metal oxides leads to an increased reactivity as they are able to react to a greater extent compared with normal crystals. Therefore, more molecules of metal oxide nanoparticles are available on the surface for the reaction of incoming molecules. Nanoscale oxides possess unique surface chemistry that is also now well established that is metal oxide nanocrystals exhibit intrinsically greater chemical reactivities compared with microcrystals and normal crystal oxides [19].

Photocatalytic materials based on metal oxide nanomaterials are now the frontliners in environmental remediation, especially in the degradation of organic pollutants in wastewater. The metal oxide-based nanomaterials with well-controlled structural, crystalline, and surface features function as semiconductors with wide band gaps and also show favourable characteristics like non-toxicity and stability in the water for photocatalytic oxidation/degradation of organic pollutants [7].

Here we discuss the outstanding performance of metal oxide nanomaterials focusing on the photocatalytic applications and their recent advancement on some of the most common metal oxide nanostructured photocatalysts TiO_2 , ZnO , CuO , Cu_2O and WO_3 . These metal oxides are promising materials for environmental remediation because they are stable, inexpensive and have high visible light driven catalytic performance [13].

2.2. Synthesis of Metal Oxide-Based Nanomaterials

There are several methods of preparing metal oxide nanoparticles. In this section, we discuss some of the highly used and significant synthetic pathways for their preparation.

2.2.1. Co-Precipitation Method

In the preparation of metal oxide photocatalyst using a co-precipitation method, the synthesis reaction is normally carried out at ambient temperature. In this method, a precipitating medium and a solution of a salt precursor (usually a metal salt like a nitrate or chloride) are used to precipitate an oxo-hydroxide form in a solvent (usually water). The corresponding metal oxo-hydroxides precipitate in water by adding a base to the solution. The commonly used precipitating media in these methods are NaOH , KOH , and $(\text{C}_2\text{H}_5)_4\text{NOH}$, by which it has been established that the morphologies and properties of the metal oxides are highly influenced by the pH of the and the nature of the alkaline solution. It is also well known that the mode and rate of introducing these alkali solutions to the reaction mixture must also be carefully considered in this method in order to come up with the desired property of the metal oxides. Surfactants are also useful and are very crucial in optimizing the surface characteristics of the produced metal oxide. Surfactants narrow the range or size of obtained nanomaterials. Most importantly, this synthesis procedure is low cost, and requires mild reaction conditions like low temperature during the procedure which are its main advantages [19,20]. ZnO was synthesized using this method with $\text{Zn}(\text{NO}_3)_2$ and K_2CO_3 as precursors [21].

2.2.2. Microemulsion

Stankic et al. [20] described the microemulsion method consisting of two immiscible liquids, the nonpolar oil and polar water. Surfactant agents aids the separation of these two liquids resulting to a water/surfactant and oil/surfactant binary systems. Using appropriate quantity of the water, oil, surfactant and the metal oxide precursor is the principle of microemulsion done by continual stirring at ambient temperature to come up with a homogenized phase. The formation of nanoparticles is done by then adding precipitating agents (may also be oxidizing/reducing agent) with persistent stirring subsequently followed by centrifugation. The recovered nanoparticles are then washed and dried. In essence, the microemulsions act as nanoreactors for the creation of nanoparticles. Disturbing the several self-assembled structures formed in the binary systems will affect the shape and size of the produced nanoparticle and is the main advantage of this method. The

disadvantage however is the necessity of several washing processes and the tendency of the produced nanoparticles to aggregate that consequently needs stabilizers. Modifications have been incorporated to overcome this problem Zhang and Gao [22] synthesized TiO₂ with a 30–50 nm particle size range using this method.

2.2.3. Hydrothermal Synthesis

Several researchers refer to this technique as solvothermal. Basically, when the solvent is water it is referred to as hydrothermal. As described in the Synthesis, Properties, and Applications of Oxide Nanomaterials, thermal decomposition of the metal complexes is done either by boiling the contents in an inactive atmosphere or in an autoclave. Agglomeration may take place so a suitable capping agent or stabilizer is added to the reaction at the proper time to obstruct the growth of the particles. The stabilizers also help in dissolution of the particles in different solvents [19].

2.2.4. Sonochemical Synthesis

A solution of the starting material is subjected to a stream of ultrasonic waves (usually between 20 kHz and 10 MHz) that cleaves the bonds of the compounds. The stream of ultrasonic waves leads to the formation, growth and then collapse of bubbles in the solution that Stankic et al. describes as acoustic cavitation. As millions of bubbles collapse in the liquid, it consequently results to the production of an excessive amount of energy that is subsequently released thereby heating the solution. The morphology and the crystal shapes of the resulting metal oxides are side to be affected by the rate at which the solution is cooled. This method is notably advantageous when it comes to producing metal oxide nanoparticles of uniform size, high purity, and high surface area. In addition, a short preparation time can be achieved using this method [19,20]. This method was used to prepare TiO₂ nanoparticles with enhanced photocatalytic activities. The enhanced photocatalytic effects were said to be credited to the cavitation by the ultrasonic waves that create a distinctive environment for the hydrolysis of corresponding hydroxide, which in this case titanium alkoxide, and the formation of seed nuclei to promote the growth of TiO₂ nanoparticles [23].

2.2.5. Sol-Gel Process

The Synthesis, Properties, and Applications of Oxide Nanomaterials describes sol-gel as a process typically used to prepare metal oxides done by the hydrolysis of metal reactive precursors (usually alkoxides in an alcoholic solution). This results in the formation of corresponding hydroxide followed by the condensation of this hydroxide to form of a metal hydroxide polymer which looks like a densely packed porous gel. Heating and drying of the gel are done that leads to a corresponding powder crystal of the metal oxide of target particle size. The produced metal oxide may be in a form of a nanoparticle, bulk material or may ultimately be oxygen-deficient depending on the heat treatment procedures done [19]. Copper oxide nanoparticles were synthesized using this method with a solution of copper (II) acetate in ethanol as precursor [24].

2.2.6. Green Synthesis

Conventional methods prepared in a laboratory set-up present a number of limitations and destructive effects such as bioaccumulation, susceptibility to human error, instability and recyclability factors just to name a few. To address these concerns, a new trend of synthesis methods has risen. Green synthesis is used to avert the formation of unnecessary and damaging side-products by resorting to dependable, sustainable, and environment-friendly methods of synthesis [25].

Biological Components for Green Synthesis

The preparation of nanoparticles using green synthesis procedure is an environment friendly bioreduction method that requires relatively low energy of activation for reactions

to occur needed for synthesis. Microbes such as prokaryotic bacteria and actinomycetes have been widely utilized in the preparation of metal oxide nanomaterials. Bacteria have been broadly exploited because they display effective capabilities in reducing metal ions. Fungus has also been widely studied for the green synthesis of nanoparticles. The presence of a variety of intracellular enzymes and proteins as reducing agents helps fungi act as better biological proxies for nanoparticle synthesis. Likewise, plant extracts may have gained most attention among biological agents as a simple, effective, inexpensive and practical of methods that is an outstanding alternative to the traditional process for the preparation of metal oxide nanoparticle. Plants contain biomolecules such as carbohydrates, proteins, and coenzymes that show potential in reducing metal salt into nanoparticles [25]. For example, the green synthesis of CuO nanoparticles using plant extracts for the reduction of copper salt has displayed advantages over the use of microbes because it does not require cell culture maintenance and it also has high probability to be scaled up for large-scale synthesis [26].

The main disadvantages of the biological components for green synthesis compared to other methods are that it is difficult to achieve the desired size and morphology of the nanoparticles and it also has a considerably lower yield. The process is also commonly slow taking several hours to a few days per preparation. Moreover, a possibility of decomposition of the nanoparticles produced is highly probable owing to its bio-compatibility. Nevertheless, this method stays an attractive means of nanoparticle production [20].

Solvent System-Based Green Synthesis

Solvent systems are an important factor in the synthesis process, may it be a “green” synthesis procedure or not. The use of water as a solvent is most desirable however limitations are still met on its use on a case-to-case basis. New trends that are ionic and supercritical liquids have arisen to address the issues regarding the role of toxic/non-toxic solvents in nanoparticle production and renewable sources. Numerous metal catalytic materials, polar organic compounds, and gases are readily dissolved in ionic liquids and that fact is one advantage of using this liquid as an alternative to other solvents. Ionic liquids also allow a wide temperature range during operation since most metals melt at high temperatures (300–400 °C). Ionic liquids, although having polarity closer to alcohol, are still considerably non-coordinating against polarity which means can be hydrophobic or hydrophilic depending on its cation or anion. Furthermore, they have no vapor pressure hence evaporation into the environment is not an issue. They also function as both anion and cation. Similarly, supercritical fluids are made from ordinary solvents that are subjected to temperatures and pressures beyond their critical point. The properties of these solvents such as density, viscosity, and thermal conductivity, are drastically altered when they are in the supercritical state. The alterations on their properties offer remedy to the initial limitations of ordinary liquids [25].

2.3. Applications of Metal Oxides

The unique physical and chemical properties of metal oxide nanostructures lead to its use in a huge variety of applications including the removal of heavy metals, poisonous gas sensing, textile coating for wearable electronic devices, biomedical applications, and photocatalytic degradation of organic contaminants, among others [27,28]. In this section, we lightly discuss these applications.

2.3.1. Removal of Heavy Metals

Pollution by heavy metals has received major attention because they have been found to have toxic and carcinogenic impacts to humans and the environment. Various industries like those conducts mining operations, metal plating, battery production among others, releases heavy metals wastewaters into the environment. They are non-biodegradable and tend to bio-accumulate. Just to mention a few, excessive zinc levels can result in well-known health problems which include anemia, stomach cramps, skin irritations, nausea

and vomiting. Lead can also cause damage to the central nervous system, kidneys, liver, and reproductive system. Prolonged exposure to cadmium can lead to kidney failure and exposure to high concentrations will cause death [29]. In the case of nickel, even though it is an integral component of urease, a level of $>5 \text{ mg}\cdot\text{kg}^{-1}$ per day has been found to cause human health risks [30]. Numerous techniques have been employed for the elimination of heavy metals because of the harmful effects they cause. These methods include precipitation, ion exchange, electrochemical technologies, membrane filtration and adsorption [31]. Among these methods, adsorption often generates excellent quality treated effluents. In addition, the adsorbents can be regenerated by suitable desorption processes due to the reversible nature of most adsorption processes making these adsorbents susceptible for multiple use. Thus, the adsorption process is now being adopted as a major technique in removing the heavy metal contaminants from bodies of water [32]. A study by Taman, et al. successfully synthesized CuO nanoparticles as adsorbent for the effective and fast elimination of heavy metal ions Cd(II) and Fe(III) during the wastewater-treatment process [31].

Adsorption is a physicochemical surface interaction between the adsorbate and the adsorbent. For a speedy and effective removal of heavy metals in wastewater, adsorbents should have a high surface area, desirable textural and surface features, and good mechanical stability. Nanosized metal oxides are used for adsorption processes due to the fact that they exhibit remarkable surface characteristics, microstructural features, and high surface area. The active sites and high surface area facilitate adsorption events. The surface energy of adsorbent materials is increased by reducing the size and more active sites on their surface are available for organic molecules to interact, and in this case, be adsorbed into the surface of the adsorbent thus, nanomaterials show better adsorption capacity compared to the bulkier counterparts [7].

2.3.2. Metal-Oxide Assisted Carbonization

Ronsse, et al. define carbonization as a method of converting biomass into a highly carbonaceous materials using a slow pyrolysis process. In a carbonization process, the biomass is heated in an environment with a limited to no oxygen, and reaction conditions tailored to optimize production of char [33]. The produced bio char is also known as charcoal, which is a porous, carbon-enriched, greyish black solid.

Carbonization is employed in wearable electronic devices where garments can have the capability of storing energy while still be able to retain its flexibility. Cotton is established as an innovative groundwork for smart wearable energy storage devices because of its appealing properties. Conventional approaches using either additional coating or direct carbonization present the problem that produces mechanically fragile or electrochemically poor textile. An innovation of simply coating metal oxide nanoparticle film onto cotton prior to the conventional carbonization leads to a textile with high electrochemical energy performances. Using this technique also allows excellent flexibility under repeated mechanical deformations. Lam, et al. demonstrated that the coating of metal oxide on the cotton and successive pyrolysis readily turn cotton into conductive textile with excellent porosity and toughness. The textile produced has the energy density of $2.24 \text{ m}\cdot\text{Wh}/\text{cm}^3$ (nearly 3 times higher than other commercial supercapacitors) and the power density of $585 \text{ m}\cdot\text{W}/\text{cm}^3$ (over 2-orders-of-magnitude higher than that of the lithium battery). It was shown that the carbonization assisted with metal oxide nanoparticles permits the migration of metal atoms into the graphite-like layers of the carbonized with metal oxide cotton. Notable changes in the microstructure leading to a drastic increase in both the mechanical stability and the electrochemical performance (nearly 40 times increase in terms of material toughness and 300 times increase in energy density versus the textile produced from the conventional carbonization) due to the migration of metal atoms into the resulting textile [34].

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

Over the years, metal oxide semiconductors have been employed for gas sensing such as SnO_2 , In_2O_3 , Fe_2O_3 , WO_3 , Cr_2O_3 , $\text{Co}_3\text{O}_4@CuO$, and $\text{TiO}_2@WO_3$. Toxic gases like ammonia (NH_3) need to be monitored because it is a component of atmospheric contaminants and is potentially explosive in industrial scenarios. Human exposure to NH_3 is known to induce throat irritation, itchy skin, dizziness, and fatigue, and is why its levels in homes and industries are rigorously restricted. The U.S. Department of Labor's Occupational Safety and Health Administration (OSHA) specifies an allowable concentration of 50 ppm, while the US Institute of Occupational Safety and Health (NIOSH) imposes a maximum of 25 ppm. Hence, the fabrication of high-performance ammonia gas sensors has essential practical significance for continuously monitor the living/working environment as well as the leakage of ammonia gas [35].

One sensor that has been demonstrated to exhibit especially good ammonia gas-sensing ability is a sensor based on nickel oxide (NiO). Wang et al. [35] prepared an ammonia sensor displaying excellent performance on a NiO foil substrate by using ZnO nano-biodecorated NiO nanocone to detect ammonia in the surrounding environment. These NiO-based ammonia sensors have made great progress but performance of ammonia sensing shows to be unsatisfactory that usually requires high temperatures during operation, resulting in high power usage and potential safety hazard. Recently, a sensitive and fast-responding ammonia gas sensor prepared using a TiO_2/NiO bilayer by Kumar et al. was reported to overcome the mentioned drawbacks [36]. Their work showed the ammonia gas sensing properties of TiO_2/NiO bilayer sensors has a low detection range (5–500 ppm) that can operate at a low temperature regime (30–300 °C) with fast response times (~24–30 s).

Metal oxide-based gas sensors are also used in a proposed titanium dioxide technology. The e-nose technology presents enormous potential for in site monitoring of off-odours. Usual odour measurement techniques rely on human olfactory system or conventional analytical techniques. The instrument with a non-specific gas chemical sensor is combined with a chemometric processing tool that provides a suitable technique for in site monitoring of off-odours. Romain and Nicolas however note a number of limitations are associated with the properties of chemical sensors, the signal processing performances and the real operating conditions of the environmental field. To be usable for the field measurement of off-odours, the e-nose has to deal with the lack of long term stability of these sensors. They have tested and found metal oxide-based gas sensors (Figaro type) are the best gas sensors for long term application. Employing univariate multiplicative factor exhibits the best results for complex data of in site, real-time, off-odours measurements. With real-life measurements, it is undeniably very difficult to identify a single direction in a multivariate space that is only correlated to sensor drift. So, for each sensor, an individual multiplicative factor was calculated by estimating the drift slope for a calibration gas [27].

2.3.4. Energy Conversion and Storage

Solving the world's energy and environmental crisis meant satisfying the world's growing energy demand. Researchers continue to seek sources of renewable energy in ways to reduce the carbon footprint. In the search for sustainable means to address these issues, a variety of energy storage systems have also been developed. Transition metal oxides have been extensively studied as materials for various energy conversion and storage applications.

Semiconductor metal oxides such as TiO_2 , ZnO , WO_3 , BiVO_4 and Fe_2O_3 have been found to be effective photoanodes for photoelectrochemical water splitting. Photoelectrochemical (PEC) water splitting is a solar driven water splitting method to produce hydrogen gas, which is a clean fuel having high energy density of 142 MJ/kg. This method therefore is favorable because it is environmentally friendly and sustainable with the use of solar energy. Moreover, with the innovation of nanotechnology, metal oxide nanoparticle photoelectrodes have shown better PEC performances than their bulk counterparts, due to

their large surface areas and shorter distances for diffusion. Metal oxides have also been used for solar cells. TiO_2 have been used as supporting materials in dye sensitized solar cells for a low-cost energy conversion [37]. Metal oxides are also employed in fuel cells. As an alternative to carbon materials, metal oxides with controlled introduction of oxygen vacancies are engaged as catalyst support in fuel cell operations [38]. Commercial lithium ion batteries use lithium cobalt oxide (LiCoO_2) as cathode material [39]. In addition, metal oxides have likewise been used for energy storage. An important characteristic for charge storage devices such as lithium ion batteries and supercapacitors to achieve high power density (fast charging) are electrodes with nanoporous structures to facilitate ion diffusion. Metal oxides allow engineering of its morphology to achieve this trait. Metal oxides, therefore, represent a significant class of materials for electrochemical energy conversion, storage and catalysis applications [38].

2.3.5. Biomedical Applications

Recent development in nanoscience and nanotechnology has contributed to the wide applications of metal and metal oxides nanoparticles in several field of sciences, research institutes and industries especially in energy, biomedical and environment fields of study. The strong adsorption capability exhibited by these nanoparticles significantly enhances their performance and applications [26]. Among all metal oxides, the nanoparticles of copper oxide have gained more attention due to its distinctive properties and applications. Its applications in gas sensors, waste treatment, catalysis, batteries, food preservation, high temperature superconductors, solar energy conversion, photovoltaic devices, dye removal, field emission emitters and in agriculture have been established [26]. Moreover, CuONPs showed exclusive anticancer, antimicrobial and antioxidant efficacy which renders them a promising tool for biomedical applications. Moreover, CuONPs showed antimicrobial effects. CuONPs obtained from the agar well diffusion technique against both Gram positive and Gram negative bacteria showed the toxicity of CuONPs in destroying the growth of tested pathogens. The bactericidal effects have been traced to the formation of highly reactive oxygen species such as (OH , H_2O_2 and O^{2-}) on the surface of the CuONPs which causes death to the bacteria [40]. It has also been shown that CuONPs inhibit cancer cell growth in a study by Pramanik et al. [41]. Cu_2O nanoparticles have also been employed as a highly effective non-enzymatic glucose sensor for the detection of blood glucose levels [42].

2.3.6. Photocatalytic Removal of Organic Pollutants

Transition metal oxides and their composites exhibit excellent photocatalytic activities for the photodegradation of organic contaminants. The metal oxide-based nanomaterials with well-controlled structural, crystalline, and surface features function as semiconductors with wide band gaps and also show favorable characteristics like non-toxicity and stability in the water for photocatalytic oxidation/degradation of organic pollutants [7]. The details on these metal oxide photocatalytic applications are the focus of this review and are further discussed in Section 3.

3. Photocatalytic Applications of Metal Oxides

3.1. General Mechanism

The mechanism on the photocatalytic degradation of pollutants has been previously discussed by several groups. According to a review article by Theerthagiria et al. [13], the major role of a photocatalyst in the degradation of pollutants is to accelerate the distinct oxidation and reduction processes in the presence of light. There are three general steps in the photocatalysis of the pollutants: (1) the separation of hole and electron upon light irradiation; (2) the scattering of the charge carriers on the surface of the photocatalyst; (3) the light-driven catalytic oxidation and reduction takes place on the active sites of the catalyst.

Equations (1)–(5) lists the major reactions involved in the photocatalytic degradation mechanism and these processes are illustrated in Figure 1. (1) The generation of holes (h^+) and electrons (e^-) happens at the valence band (VB) a conduction band (CB), respectively, of the photocatalyst when it is irradiated with light. The photogenerated charges moves to the surface of the photocatalytic material to initiate the needed oxidation and reduction processes, starting from (2) the reaction of h^+ and e^- with H_2O and O_2 , respectively, resulting to the formation of highly reactive radical species, O_2^- and $\bullet OH$. (3) The reaction of these radical species with the dyes and other organic molecules lead to the degradation of these pollutants [13,43]. The photodegradation process mechanism is shown in Figure 1 [43]:

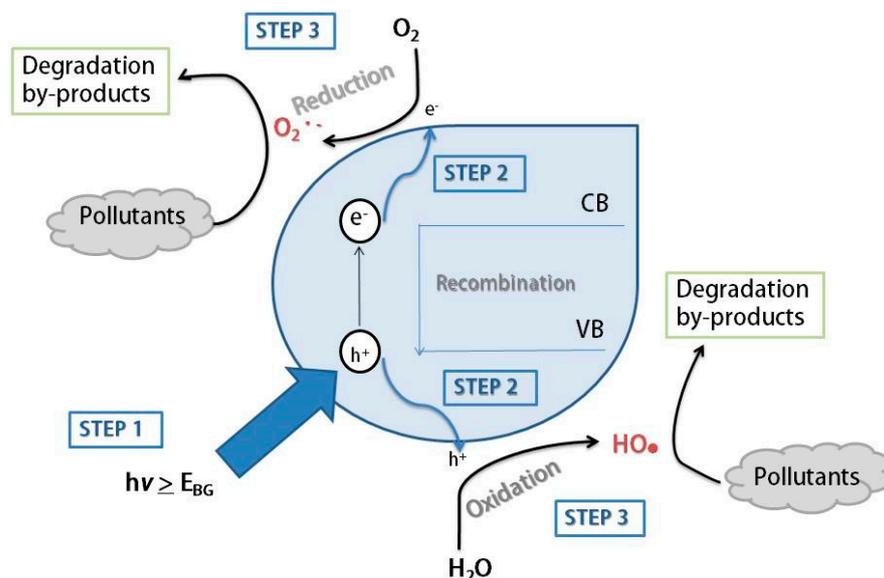
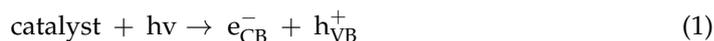


Figure 1. The mechanism of photodegradation process.

3.2. Metal Oxides in Photocatalytic Degradation

3.2.1. Titanium Dioxide (TiO_2)

TiO_2 is a widely used photocatalytic material known for its low cost, high activity, non-toxicity, chemical stability, and high resistance against photochemical corrosion [9,44,45]. Its photocatalytic activity was first reported in 1977 when Frank et al. found that TiO_2^- could effectively degrade cyanide [46]. Since then, TiO_2 has become a leading photocatalytic material used to address the issues of environmental pollution.

TiO_2 has shown notable performance in the photocatalytic degradation of pollutants. However, its photocatalytic application is also limited due to some less favorable properties which include rapid charge recombination of the photogenerated electron and hole pair, the poor sensitivity of TiO_2 under solar irradiation, reports showed that TiO_2 nanoparticles aggregate which may result to the blockage of the active site this hindering the photocatalytic activity [9,12]. These problems have encouraged researchers to engineer the TiO_2 nanoparticles to realize a more efficient photocatalytic material. Up to date, the modification of TiO_2 is among the highly studied areas in photocatalysis [12].

More recently, Li et al. [12] highlighted that the improved photocatalytic activity of modified TiO₂ is due to the reduction of the band gap of TiO₂⁻ based materials and the decrease in the rate of recombination processes between the electron and hole. Significant efforts have been made to overcome the inadequacies and to enhance the photocatalytic properties of TiO₂ nanoparticles, especially under visible light irradiation. Among them, metal ion doping was known as efficient approach since this method introduces new energy levels and thus the energy band gap can be narrowed which brought better photocatalytic activity especially in the visible light spectrum. In addition, the doped ions also introduce charge trapping sites which aids in the suppression of electron-hole recombination [12,47]. Miyamoto et al. [48] synthesized lutetium ion (Lu³⁺)-doped titanium dioxide (Lu-TiO₂⁻) by a sol-gel method. When used in the photocatalytic decomposition of adenosine 5'triphosphate (ATP) under UV irradiation, the Lu-TiO₂ nanoparticles performed better than those of the undoped TiO₂. Xie et al. [47] prepared doped the TiO₂ nanoparticles with Selenium ion (Se⁴⁺). The Se-doped TiO₂ nanoparticles were synthesized using sol-gel method and were used in photo degradation of aqueous Rhodamine B (RhB) under visible light irradiation. The obtained results showed that compared to pure TiO₂ nanoparticles, Se-doped TiO₂⁻ exhibits better photocatalytic properties brought by a narrowed band gap upon doping with Se⁴⁺ ions.

Another way to enhance the photocatalytic performance of TiO₂ is by depositing metals or metal oxides on the surface of the TiO₂. According to studies, loading noble metals such as Au, Ag, Pt, and Pd have been effective in reducing the rate of charge recombination since these metals acts as electron acceptors [49]. Jaafar et al. [49] deposited metallic silver (Ag⁰) nanoparticles on the surface of TiO₂ nanoparticles via in-situ electrochemical method. The prepared Ag-TiO₂ nanoparticles was used in the photodegradation of chlorophenol which resulted to 94% photodegradation rate after 6h. The authors characterized that the success in the photocatalytic degradation was influenced by the amount of Ag⁰ and the electron trapping sites which enhanced the electron-hole separation. Shan et al. [50] fabricated a set of biochar-couple Ag and TiO₂ composites by mixing, calcination, and post-deposition method. The photocatalytic properties of the resulting composites were tested in the removal of methyl orange (MO) as a representative pollutant. Compared with the pure TiO₂, the TiO₂ catalyst modified with Ag showed better photocatalytic performance, evidenced by the highest decolorization (97.48%) and mineralization efficiency (85.38%). The enhanced photocatalytic performance is attributed to the effective promotion of the electron-hole charge separation. In addition, the photocatalyst showed high stability up to five photodegradation cycles. Harja et al. [51] developed TiO₂-Pd photocatalyst by doping TiO₂ with Pd using wet impregnation method. The photocatalytic properties of TiO₂-Pd were examined in the heterogeneous photodegradation of chlorific acid (CA) as a target pollutant. Accordingly, the authors reported the optimal experimental condition (0.2 g/L catalyst, 5 mg/L CA, 6.2 m·W/cm² irradiation flux) in which TiO₂-Pd photocatalyst completely removed the target pollutant. This efficient photocatalytic activity of the TiO₂-Pd is also confirmed by 65% mineralization yield.

Metallic elements are effective aids in enhancing the photocatalytic properties of TiO₂ nanoparticles by reducing charge recombination, inducing a band gap shift, and enhancing the photocatalytic activity under visible light irradiation. However, the preparation of metal-doped photocatalysts is costly, especially for those catalysts employing noble metals. In addition, metal-doped photocatalysts is prone to photo-corrosion during the photocatalytic process. To address this issue, the use of nonmetals like carbon, nitrogen, and sulfur, has become an interesting in developing photocatalysts that are efficient in the visible light region [52,53]. Liu et al. [52] showed the 60% efficient removal of diclofenac was achieved using iodine-doped TiO₂ (I-TiO₂) nanomaterials under 2 h or visible light irradiation. Only 10% removal was achieved using pure TiO₂ under the same experimental condition. The characterization of the photocatalysts showed that the doping of non-metal does not only extends the photocatalytic reaction up to the visible light region, but also aids in promoting charge carrier separation. Xiong et al. [53] prepared S-TiO₂ films by doping

TiO₂⁻ films with sulfur. They reported compared with undoped TiO₂ films, the S-TiO₂ films showed better photocatalytic performance for the degradation of methylene blue (MB) even though the two films have the same surface area. The improved photocatalytic activity is due to the higher porosity, bigger pores, more hydrophilic surface, and a red shift in the bandgap brought by the S dopant [53,54]. Wang et al. [55] synthesized mesoporous C, N-co doped TiO₂ hybrid shells combined with graphite carbon. The prepared hybrid shells were used in the photodegradation of organic dyes subsequently showing better photocatalytic performance than that of pure TiO₂ under the visible light. The enhanced photocatalytic activity is attributed to the improved visible light absorption and charge separation efficiency.

Among the developing research interests that aim to enhance the photocatalytic activity of TiO₂ is the immobilization of TiO₂ on a carrier like metallic oxides, activated carbon, and other carbon materials. Loading the TiO₂ on these materials are known to effectively address the problems of pure TiO₂ photocatalysts [56,57]. Recently, Saqib et al. [58] investigated the photocatalytic activity of TiO₂ nanoparticles immobilized on zeolite which was prepared by liquid impregnation method. The results of the experiments portrayed the methylene blue dye degraded at a rate four times faster when a pure TiO₂ was employed as a photocatalyst. Zhu et al. [59] reported the performance of the photocatalytic material Mn-TiO₂/Sepiolite, prepared using the sol-gel method and calcined at 400 °C gave a 98% degradation rate of emerald green dye under visible light irradiation. In addition, this Mn-TiO₂/Sepiolite exhibits good stability even after five cycles of photocatalysis. Another interesting material for TiO₂ modification is Biochar (BC), a type of carbon material which can be derived from biomass pyrolysis, which is among the carbon materials that gained significant interests in many fields [56]. A TiO₂/BC catalyst prepared by Zhang et al. [60] via a sol-gel method showed a 97% degradation rate of reactive brilliant blue KN-R dye in wastewater. Ramos et al. prepared TiO₂/GO composites using sol-gel and improved Hummers method and the photocatalytic activity of the composite was tested in the photodegradation of azo dyes under UV and solar irradiation. Under UV radiation, a degradation rate of 20% was achieved while a 63% degradation rate was obtained with solar radiation. On the other hand, Fu et al. [61] employed the sol-gel method to fabricate graphene oxide/TiO₂ (GO/TiO₂) composites whose photocatalytic properties surpassed that of the pure TiO₂, resulting in a 95.8% degradation rate of methylene blue after 2.5 h.

Another successful method is improving the photocatalytic performance of TiO₂ is combining it with another semiconductor to develop a heterojunction. This method does not only promote electron-hole charge separation but also expands the photocatalytic response throughout the visible region and even in the near infrared region [12]. Liu et al. [62] used TiO₂ nanoparticles to modify Bi₂MoO₆ nanocrystals using solvothermal-calcination method which was shown effective in enhancing the visible light-driven photocatalytic activity of BiMoO₆ removal of antibiotics in aqueous solution. This is attributed to the presence of the TiO₂ nanoparticles whose CB serves as the electron transfer platform which promotes efficient charge separation at the TiO₂/Bi₂MoO₆ heterojunction interface. Using the TiO₂/Bi₂MoO₆ heterojunction, the degradation rate of ciprofloxacin, tetracycline, and oxytetracycline reached 88%, 78%, and 78%, within 150 min under visible light. Recently, Abbas et al. [63] showed a near-complete degradation of cefazolin, a compound found in drinking water, using a nanoheterojunction photocatalyst of spherical titanium dioxide (TSN) over ZSM-5 zeolite. The prepared TSN@ZSM-5 mesoporous also exhibited excellent stability and maintained its high photocatalytic performance even after several cycles of use. The overall results of the experiments portrayed the potential of this nanoheterojunction photocatalyst in wastewater treatment.

3.2.2. Zinc Oxide (ZnO)

In recent years, the unique and highly favorable properties of ZnO nanomaterials have attracted valuable research attention in the field of photocatalysis, gas sensing, renewable energy production and energy storage, among others [32,64]. As a low-cost, nontoxic and

an environment friendly material, ZnO nanoparticles are known to compete well with TiO₂ and modified TiO₂ when it comes to visible light-driven photocatalytic degradation of organic pollutants. In fact, compared to TiO₂, ZnO is reported to exhibit a broader range of solar response in the visible light spectrum [4]. A type II-IV semiconductor ZnO has a wide band gap of ~3.37 eV a large exciton binding energy of 60 meV, effective ultraviolet absorbance and good chemical stability, rendering its potential in photocatalytic processes [4,65,66]. The synthesis of ZnO photocatalytic material can be carried out through hydrothermal synthesis, homogeneous precipitation, sol-gel method and other various reported techniques [67].

Chen et al. [67] reported the photocatalytic activity of ZnO nanoparticles (NPs) prepared by a sol-gel method. The photocatalytic activity of ZnO NPs were checked using the degradation of MO, CR, and DB38 azo dyes in which the results displayed that the removal rate of azo dyes increased with increased amount of dosage of catalyst and decreased initial concentration of azo dyes. Balcha et al. [68] discussed the photocatalytic activity of ZnO nanopowder prepared by precipitation and sol-gel method. The photocatalytic behavior of the prepared nanomaterials was investigated under the UV light driven photocatalytic degradation of aqueous methylene blue dye as a representative organic contaminant in water. The experimental results revealed that with the optimum photocatalyst load of 250 mg/L, photodegradation efficiencies of 81% and 92.5% were achieved using the nanomaterials prepared by precipitation and a sol-gel method, respectively.

The highly efficient performance of ZnO photocatalyst in heterogeneous photocatalysis reaction requires a suitable architecture and structure that lessens the loss of photo-generated electron loss during excitation state and boosts photon absorption. Significant number of approaches have been explored aiming to enhance the photocatalytic properties of ZnO under visible light irradiation. Among these, doping of ZnO with metals and metal ions has become a famous technique among researchers. This approach has been shown effective in reducing the competing electron-hole recombination consequently leading to a better photocatalytic property compared to the undoped ZnO [64,65,69].

Ba-Abbad et al. [69] reported the enhanced photocatalytic activity of ZnO when doped with Fe³⁺. The Fe-ZnO nanomaterial was synthesized using sol-gel method and used as a photocatalyst in a solar light-driven degradation of 2-chlorophenol in aqueous solution as a model organic pollutant. In comparison to the pristine ZnO, the as-prepared Fe-ZnO showed better photocatalytic performance attributed its smaller crystallite size and lower energy band gap. A 93% and 73% degradation efficiency of methylene blue (MB) dye and 4-chlorophenol, respectively, was reported by Khan et al. [70] using Fe³⁺-doped ZnO (Fe_{0.8}-ZnO) prepared by sol-gel method. The authors reported that the higher photocatalytic activity of Fe_{0.8}-ZnO is brought by higher surface area, extended light absorption longer wavelength, and reduced rate of charge recombination. Shirdel et al. [65] synthesized ZnO and Ba-doped ZnO (Ba/ZnO) using a sol-gel method. The group investigated the photodegradation of rhodamine B using the prepared photocatalysts under visible light illumination and successfully achieved 98.40% removal efficiency using Ba/ZnO within 68 min of irradiation under mild alkaline condition. Recently, high efficiency and outstanding reusability Ba-doped ZnO thin film (ZBO) photocatalyst was reported by Jayakrishnan et al. [71]. A 96% efficiency was achieved by Zn_{0.9}Ba_{0.1}O in the removal of rhodamine B (RhB) dye within 60 min of irradiation. A series of characterization revealed that the outstanding performance is brought upon by the highly efficient charge generation accompanied by highly favored separation of charge carriers. Moreover, this photocatalyst showed no significant change on its performance over six cycles of photocatalytic applications, proving its high stability. Wang et al. [72] fabricated Zn/ZnO composite photocatalyst by a simple hydrothermal method and reported a 90% degradation efficiency of methyl orange (MO). Under the same photodegradation conditions, pure ZnO only showed 10% efficiency due to its less efficient charge separation compared to that of Zn/ZnO composite.

A carbon fiber (CF)-based photocatalyst, named Pt@ZnO NRs/CFs, fabricated by Gu et al. [73] was reported to exhibit improved photocatalytic performance than that of ZnO NRs/CFs when used as a photocatalyst in the degradation of methyl orange (MO) solution attributed to the cooperative effect between the Pt nanoparticles and ZnO nanorods. The reported degradation rates are 72% and 99.8% for ZnO NRs/CFs and Pt@ZnO NRs/CFs, respectively. Moreover, this novel hierarchical photocatalyst was tested to have good stability and can be used repeatedly in several photocatalysis cycle. Buera et al. [74] prepared a nanocomposite of Ag-decorated ZnO-graphene (GZAg) using a hydrothermal process. This photocatalyst was then used in the photodegradation of methyl orange under UV and solar illumination achieving. Accordingly, using GZAg hybrid composite, a photodegradation rate of 95.6 was reached after 6 h or UV irradiation while 98.9% was attained only in 3 h under solar irradiation. On the other hand, under the same experimental conditions, the undecorated graphene-ZnO (GZnO) only attained degradation rates of 77% and 91.8% under UV and solar irradiation, respectively. The excellent performance of GZAg is attributed to the enhanced absorption of visible light and enforced charge transfer as a results of Ag loading.

Another attractive approach in the development of modified-ZnO photocatalyst is to immobilize the ZnO NPs on the polymer supports. Studies revealed that desired photocatalytic performance are achieved with ZnO/polymer nanocomposite [66,75]. Qiu et al. [66] reported a complete degradation of rhodamine B using/poly (fluorene-co-thiophene) (PFT) nanocomposite under visible light irradiation. This nanocomposite also showed a 40% removal of phenol and methyl orange under the same experimental condition. The characterization of the as-prepared nanocomposite revealed the enhanced response in the visible spectrum with expansion of the light absorption range up to 500 nm as compared to 387 nm of the pure ZnO. In a recent study, a hybrid system composed of ZnO and poly (methylmethacrylate) nanoparticles (PMMA-NPs) PMMA was synthesized by Di et al. [75]. The photocatalytic activities of the resulting novel inorganic/polymeric hybrid nanomaterials were evaluated in the photodegradation of methylene blue dye and sodium lauryl sulfate surfactant under UV light radiation. The results showed the that these novel inorganic/polymeric hybrid nanomaterials are active as photocatalysts and are promising candidates in the wastewater treatment.

When coupled with other semiconductors such as TiO₂, WO₃, and SnO₂, the photocatalytic activity of ZnO is highly enhanced. Muguthan et al. [76] fabricated a ZnO-WO₃ mixed oxide catalyst which exhibits efficient photocatalytic degradation of diclofenac, a pharmaceutical compound commonly found as a water pollutant. The prepared mixed oxide nanomaterials displayed 76% mineralization of diclofenac under visible light irradiation, a better photocatalytic performance compared to the pure ZnO. In addition, this nanomaterial showed high stability and no significant change on the photocatalytic performance even after several cycle of photodegradation process. Sharma et. al. [77] reported the promising photocatalytic performance of copper oxide/zinc oxide-tetrapods (CuO/ZnO-T) nanocomposite prepared by a hydrothermal process. A series of characterization of this nanocomposite reveals its high porosity, large surface area, and low band gap which resulted in excellent photocatalytic performance in comparison to pure ZnO-T. The CuO/ZnO-T nanocomposite attained a photodegradation efficiency of 80% and 86% for Reactive yellow-145 and Basic violet-3, respectively. Moreover, the nanocomposite also showed excellent performance in the removal of heavy metals, achieving an adsorption capacity of 99% and 97% in the removal of chromium (VI) and lead (II). The results of the conducted study proved that CuO/ZnO-T nanocomposite exhibits a high potential in the photocatalytic removal of various wastewater contaminants. A recent study on CuO supported on ZnO (xCu/ZnO) photocatalyst was prepared by Acedo-Mendoza et al. [78] and was reported to reach 99% degradation efficiency of methyl orange (MO) dye under UV irradiation. Compared to the pristine ZnO, the excellent performance of the prepared xCu/ZnO photocatalyst is due to the presence of the copper oxide which acts as the electron trap that inhibits the recombination between the photogenerated electrons and holes.

3.2.3. Tungsten Oxide (WO₃)

Tungsten oxide (WO₃) is among the inexpensive semiconductors that show promising photocatalytic performance. It exhibits highly tunable stoichiometries and structures, good response to solar spectrum due to its narrow band gap which measures 2.5–3.0 eV [79], Earth-abundance, and thus, its photocatalytic activity under visible light is well known [79,80]. In addition, WO₃ has low toxicity, stable physicochemical properties and high oxidizing ability of the holes in the valence band [13]. In addition to photocatalysis, WO₃ is an important material in many other applications, including dye-sensitized solar cells (DSSCs), sensors, photoelectrochemical water splitting, and high T_c superconductivity, among others [79–82].

A promising photocatalytic removal of organic water contaminants by WO₃ under UV irradiation was reported by Mohagheghian et al. using diazinon as a model pollutant. In addition, the WO₃ photocatalyst displayed effective photocatalytic activity and stability even after five successive cycles [83]. On the other hand, Nguyen et al. investigated the photocatalytic performance of WO₃ in the degradation of amoxicillin (AMO) under simulated solar illumination. A complete removal (99.99% photodegradation rate) of AMO was achieved under optimal condition [84].

Despite showing promising photocatalytic properties, the photocatalytic efficiency of WO₃ has been limited mainly because of rapid recombination of photo-generated charge carriers and relatively low CB level lies above the reduction potential of O₂/O²⁻ resulting to less reduction of the O₂ molecule during the photocatalytic degradation process [13,79]. These reasons have pushed researchers to realize several promising techniques that would fine tune the structure and energy band gap to WO₃ subsequently resulting to much improved photocatalytic performance. Among the efficient techniques are morphology control, noble metal deposition, element doping, and coupling with another semiconductor to form a heterojunction [13].

A significant number of studies have been reported which focused on the morphology control of WO₃ aiming to enhance the photocatalytic applications of WO₃ [85–87]. Yao et al. [88] fabricated a novel WO₃ hierarchical structure composed of many nanosheets through a facile and surfactant-free hydrothermal method. The photocatalytic performance of the resulting WO₃ products were investigated in the photocatalytic degradation of three organic dyes namely methylene blue (MB), eosin red (ER) and Congo red (CR). The results showed that the prepared novel WO₃ hierarchical structures exhibit promising photocatalytic properties. Also, the same group reported a highly efficient degradation of organic dyes under visible light irradiation by employing WO₃ nanorods prepared by facile one-step hydrothermal method. MB, ER, and CR were also employed as the model organic materials to investigate the photocatalytic activity of WO₃ nanorods. As a result, the degradation rate of the dyes is 93.1%, 86%, and 80% for MB, ER, and CR, respectively, proving that WO₃ nanostructures are promising candidates for wastewater treatment [89]. Just recently, the performance of WO₃ nanorods in the photocatalytic degradation of rhodamine B dye was investigated by Govindaraj et al. [85]. The nanorods were fabricated using simple hydrothermal method with Na₂SO₄ as a structure-directing agent (SDA). The fabricated nanorods were subjected to a series of characterization tests revealing that the SDA-WO₃ exhibits low photoluminescence intensity which could improve the electron-hole pair separation and decrease the rate of charge recombination process. Adhikari et al. [87] fabricated WO₃ nanostructures with different morphologies (nanoparticles and nanorods) using a simple solution precipitation method. The obtained nanostructures were used in the visible-light-driven photocatalytic degradation of rhodamine B (RhB). The experimental results showed that the nanorods displayed better photocatalytic properties than the nanoparticles which could be attributed to the higher adsorption rate of RhB on the surface of the WO₃ nanorods. An excellent photodegradation rate of 99% was attained after 5 h of exposing RhB unto visible-light photocatalysis. Moreover, Liang et al. [90] synthesized two-dimensional (2D) ultra-thin WO₃ nanosheets with dominant reactive {002} crystal facets. These nanosheets displayed remarkable performance in xylene sensing

and in the photocatalytic degradation of methyl orange which could be attributed to the high percentage of reactive {002} crystal facets and high surface area. These results clearly show that the performance of the photocatalysts is influenced by the morphology and that morphology control is an effective technique in improving the photocatalytic activity.

Several studies have been focused on doping the WO_3 with metals aiming to improve the photocatalytic activity of the metal oxide photocatalyst. The effect of Ni doping on the properties and photocatalytic activity of WO_3 photocatalyst was investigated by Mehmood et al. [91] wherein they employed a chemical co-precipitation method in the fabrication of Ni-doped WO_3 nanoplates. A series of characterization methods were applied revealing that doping Ni into WO_3 resulted in a narrowed band gap and reduced rate of unwanted charge recombination processes. As a result, the prepared nanoplates were reported to exhibit 96% mineralization of methyl red after 2 h of visible-light driven photocatalytic degradation, much higher than that of pure WO_3 photocatalyst. Zhang et al. [92] reported the comparison between the photocatalytic activity of flower-like WO_3 and Ag@WO_3 . The Ag@WO_3 , which was prepared by depositing Ag nanoparticles on the petals of the WO_3 , displayed a significantly higher photocatalytic performance over WO_3 nanoflowers on the degradation of MB and 2-chlorophenol dyes over WO_3 flowers. This is attributed to the enhanced absorption of visible light and faster rate of charge separation brought upon by the deposition of Ag nanoparticles. Dhanalakshmi et al. [93] synthesized a novel iridium-loaded WO_3 (Ir/WO_3) nanocomposite using a single step hydrothermal process. The photocatalytic performance of the as-prepared Ir/WO_3 nanocatalyst were checked in the visible light-driven photodegradation of crystal violet (CV) and methylene blue (MB) dye as the model organic pollutant. As a result, the Ir/WO_3 nanocomposite exhibited higher photodegradation efficiency on CV and MB compared to pure WO_3 attributed to the reduced rate of charge recombination when Ir was anchored on WO_3 .

Graphene, graphene oxide (GO) and other carbon-based composite materials have displayed promising performance in various fields such as energy-related applications and environmental remediation. In a study on modification of tungsten oxide (WO_3) photocatalyst, Sajjad et al. [94] showed that the photocatalytic activity of WO_3 can be significantly improved when aided with GO. Their group reported the successful preparation of GO and WO_3 composite for as a photocatalyst under visible light irradiation. The prepared composite was characterized to have a favorably low band gap and a promising response under the visible spectrum. Kottam et al. [95] successfully modified a monoclinic tungsten oxide ($m\text{-WO}_3$) with carbon nanodots (g-CDs) prepared by green synthesis using a hydrothermal method. The prepared g-CDs/ $m\text{-WO}_3$ system was employed in the photocatalytic degradation of the crystal violet dye giving an efficiency of 95%. Also, the photocatalyst system exhibited good reusability as its performance was not significantly changed even after four repeated cycles. Troung et al. [96] investigated the performance of $\text{C}_3\text{N}_4\text{-WO}_3$ composite nanosheet (nsCW21) under visible light-driven photocatalytic degradation of natural organic matter (NOM). According to their results, the nsCW21 photocatalyst displayed higher degradation efficiency compared to the bare WO_3 photocatalysts. When H_2O_2 was employed as a cocatalyst, a 71% removal rate was achieved after 5h of irradiation. Also, nsCW21 displayed good stability and still exhibited considerably efficient photocatalytic performance during five cycle.

Coupling WO_3 with other semiconductor is among the booming research interest in order to maximize the photocatalytic applications of WO_3 . Xie et al. [97] employed a hydrothermal-solvothermal method in preparing a novel $\text{In}_2\text{O}_3/\text{WO}_3$ heterostructured photocatalyst in response to wastewater purification. Compared to pure WO_3 , the obtained $\text{In}_2\text{O}_3/\text{WO}_3$ photocatalyst displayed 3.70 times higher photocatalytic performance towards organic dyes. Moreover, this novel photocatalyst was confirmed to exhibit high photostability and displayed a photodegradation efficiency of 86.6% and 86.4% for methylene blue and rhodamine B, respectively, even after three cycles. More recently, the potential of elsmoreite/tungsten oxide@ZnS photocatalyst in the degradation of pharmaceutical and personal care products (PPCPs) was recently reported by Czech et al. [98]. They re-

ported that elsmoreite/tungsten oxide@ZnS heterojunction exhibited a photodegradation efficiency of 20–70% of the selected PPCPs. In addition, this photocatalyst showed good stability and recyclability.

3.2.4. Copper Oxide Photocatalyst (Cu_2O and CuO)

Among the most promising candidates as a photocatalytic material for use in degradation of organic pollutants are copper oxide nanoparticles, known to possess favorably high optical absorption and optimal band gap. Copper oxides can be fabricated at low cost with its raw materials present in high abundance in Earth's crust. Copper oxide has two semiconducting phases: cuprous oxide (Cu_2O) and cupric oxide (CuO) both p-type semiconductors that possess a band gap of 2.12 eV and 1.6 eV, respectively [99].

The applications of these oxides in environmental remediation, particularly in photocatalytic degradation of organic pollutants has been reported in several studies [26,99–101]. For example, just recently, Muthukumaran et al. [102] fabricated Cu_2O NPs using a solvent-free route green synthesis process. The as-synthesized Cu_2O NPs were subjected to a series of characterization tests and then evaluated for their photocatalytic activity. A series of experiments revealed that these nanomaterials exhibited a favorable photocatalytic efficiency which is attributed to the reduction of the charge recombination rate. The effectiveness of the photocatalytic behavior of the synthesized nanoparticles were also verified when used as the photocatalytic material in the degradation of methylene blue.

However, the unfavorable rate of the recombination between the photogenerated holes and electrons competes with the photocatalytic activities of Cu_2O and CuO . In addition, these copper oxide NPs are also prone to photocorrosion. For instance, upon exposure to light, Cu_2O can be converted into CuO via a photooxidation process which is known to deactivate the photocatalytic mechanism [99,100]. In order to address these limitations, valuable ideas have been generated and has brought significant improvement on the properties of copper oxide photocatalysts.

Morphology control is among the known method in improving the photocatalytic performance of copper oxide photocatalysts. Prado-Chay et al. [103] synthesized cuprous oxide (Cu_2O) microspheres using a simple chemical method. The photocatalytic activity of the resulting photocatalyst was evaluated using the photodegradation of methyl orange as a model. As a result, a photodegradation efficiency of 76% was achieved using the porous Cu_2O microspheres. According to the conducted characterization, the improved photocatalytic performance under visible light is due to the increased porosity of the prepared photocatalyst.

The use of carbon-based composite materials in the engineering of copper oxide materials has displayed promising performance in the field of photocatalysis. Polat [104] fabricated a two-dimensional thin film catalyst from a cuprous oxide sputtered on a monolayer of graphene for visible light-driven photocatalysis. The prepared $\text{Cu}_2\text{O}/2\text{D}$ graphene thin film catalyst was used for the degradation of hydrogen peroxide under simulated visible irradiation. As a result, the $\text{Cu}_2\text{O}/2\text{D}$ graphene catalyst displayed a photocatalytic activity 16 times higher than that of the neat Cu_2O . Karthikeyan et al. [105] synthesized a hierarchical Cu_2O nanospheres and a Cu_2O on reduced graphene oxide ($\text{Cu}_2\text{O}/\text{rGO}$) with a Pompon Dhalia-like morphology using a one-pot synthesis method. When used in the photodegradation of 4-chlorophenol, the $\text{Cu}_2\text{O}/\text{rGO}$ displayed an efficiency of 95% within 1 h. This is much higher compared to the degradation efficiency of pure hierarchical Cu_2O , attributable to increased photoresponse under the visible spectrum. Su et al. [106] reported another potential modification of cuprous oxide in the form of $\text{Cu}_2\text{O}/\text{Cu}/\text{rGO}$ @carbon nanomaterial ($\text{Cu}_2\text{O}/\text{Cu}/\text{rGO}$ @CN) which were successfully fabricated using hydrogel method. As reported, the introduction of the reduced graphene oxide significantly enhanced the photocatalytic activity of $\text{Cu}_2\text{O}/\text{Cu}/\text{rGO}$ @CN towards the degradation of *p*-nitrochlorobenzene under visible light illumination. The $\text{Cu}_2\text{O}/\text{Cu}/\text{rGO}$ @CN exhibited efficient charge transport process and reduced charge recombination.

Recently, an all-solid-state Z-scheme is gaining attention for the degradation of environmental pollutants. Particularly, a number of studies have been published on which the photocatalytic activity of Cu_2O catalyst is highly enhanced by using the Z-scheme modification [105–108]. Shen et al. [107] presented a systematic investigation of the reduced graphene (RGO)-based composites, RGO- Cu_2O and RGO- $\text{Cu}_2\text{O}/\text{Bi}_2\text{WO}_6$. Accordingly, the RGO- $\text{Cu}_2\text{O}/\text{Bi}_2\text{WO}_6$ composite showed the highest photocatalytic performance of 86% in the degradation of tetracycline which is about three times higher than the performance of the pure Cu_2O and six times higher pure Bi_2O_6 . Chen et al. [108] successfully synthesized a Z-scheme Cu_2O -(rGO- TiO_2) photocatalyst for the removal of 2,2',4,4'-tetrabromodiphenyl ether (BDE47) under visible light. The characterization of the prepared photocatalyst revealed that the addition of the reduced graphene oxide has favorably improved the redox ability of Cu_2O - TiO_2 system by boosting the charge transfer process resulting to a significant photocatalytic removal of BDE47.

A significant number of studies have shown the outstanding performance of CuO in the photocatalytic degradation of pollutants. For instance, Vaidehi et al. [109] reported a 97% photodegradation of crystal violet dye using monoclinic crystalline CuO nanoparticles under visible light irradiation. Rao et al. [110] synthesized CuO nanorods using a surfactant-assisted chemical precipitation method and used the obtained nanorods in the photodegradation of reactive black 5 (RB-5) in aqueous solution. As a result, a 98% degradation was achieved within 6 h or visible light irradiation. However, just like the Cu_2O , the application of CuO is also limited due to the concerns regarding the recombination processes and photocorrosion, hence, several techniques were employed to address these issues [99].

Just like in Cu_2O , modifying the CuO photocatalysts with a carbon-based material is also an attractive approach. A 99% degradation of 2,4-dimethylphenol was reported by Sharma et al. [111] using copper oxide/graphitic carbon nitride assisted with H_2O_2 ($\text{CuO}/\text{g-C}_3\text{N}_4/\text{H}_2\text{O}_2$) photocatalyst under 2 h of visible light irradiation. Kavitha et al. [112] presented a green synthesis of copper oxide nanoparticles decorated with graphene oxide (GO-CuO) whose photocatalytic activity was investigated towards the degradation of methylene blue dye. Accordingly, a photodegradation efficiency of 83.20% was recorded using GO-CuO, significantly higher paralleled to the performance of pure CuO nanoparticles.

When coupled with other semiconductor, a significantly enhanced photocatalytic activity of CuO is often achieved. Lu et al. [113] reported the photocatalytic performance of CuO/TiO_2 composite prepared by hydrolysis method using the copper obtained from aquatic plant *Eichhornia crassipes*. The obtained CuO/TiO_2 composite was used in the photocatalytic degradation of phenol, resulting to a complete removal of phenol after 80 min and 120 min under UV and visible light illumination, respectively. Sharma et al. [77] engineered copper oxide/zinc oxide-tetrapods ($\text{CuO}/\text{ZnO-T}$) nanocomposite fabricated using hydrothermal process. The $\text{CuO}/\text{ZnO-T}$ was characterized to be highly porous with large surface area and low energy band gap. When used in the removal of Reactive yellow-145 (RY-145) and basic violet-3 (BV-3) dye from aqueous solution, a photodegradation efficiency of 80% and 86% was achieved for RY-145 and BV-3, respectively. Moreover, the $\text{CuO}/\text{ZnO-T}$ nanocomposite displayed excellent performance in the photocatalytic removal of toxic heavy metal contaminants with 99% and 97% removal efficiency for chromium (VI) and lead (II), respectively. Masudy-Panah et al. [99] fabricated a series of novel CuO film photocatalysts, (a) $\text{CuO}:\text{Pd}$, (b) $\text{CuO(N)}-\text{CuO}:\text{Pd}-\text{CuO}$, and (c) $\text{CuO(N)}-\text{CuO}:\text{Pd}-\text{CuO}-\text{TiO}_2-\text{AuPd}$ with improved photocorrosion stability, reduced charge recombination, and higher photocatalytic activity towards methylene blue dye under sunlight irradiation compared to unmodified CuO. Notably, an excellent photostability of 95% after 6 h was recorded for $\text{CuO(N)}-\text{CuO}:\text{Pd}-\text{CuO}-\text{TiO}_2-\text{AuPd}$ photocatalyst. In a recent study, Sabzehei et al. [100] reported the effect of composite formation of $\text{CuO}-\text{Cu}_2\text{O}$ with TiO_2 and ZnO towards visible light-driven photocatalytic degradation of methylene blue dye. The $\text{CuO}-\text{Cu}_2\text{O}-\text{ZnO}$ composite displayed a highly reduced photoluminescence intensity signifying a better charge separation in comparison to the other composite systems. Accordingly, the

use of CuO-Cu₂O-ZnO composite as a photocatalyst resulted in a relatively complete photodegradation of methylene blue dye after 3 h of visible light irradiation.

To complete an exhaustive literature review, it worth covering titanate salts of polytitanic acid synthetization in form of nanostructures another variety concerning crystallinity, morphology, size, metal content, and surface chemistry. That can be utilized for heterogeneous catalytic, photocatalytic, photovoltaic, and energy storage applications. [114]. Molecular-level insights into photon-initiated events occurring at TiO₂ surfaces is studied in. [115,116], which covered: (1) photon absorption, (2) charge transport and trapping, (3) electron transfer dynamics, (4) the adsorbed state, (5) mechanisms, (6) poisons and promoters, and (7) phase and form. Also, gold ion and clusters stabilized in titanate framework can play a role in photochemistry transformation of methane and CO₂ [117,118].

4. Conclusions

As a consequence of global urbanization, various contaminants are released directly and indirectly into the environment. Studies on environmental remediation are now highly advocated to negate the harmful effects and to build a sustainable environment as the world moves forward on its technological advancement. For decades, metal oxides have received much attention because of their physical and chemical properties and they are now considered the frontrunners in environmental remediation, especially in the photocatalytic degradation of organic pollutants in wastewater.

This review article has presented some of the most recent developments on some of the most well-known photocatalysts, namely TiO₂, ZnO, WO₃, CuO, and Cu₂O. Modifications of the metal oxides can be made by several techniques, both by chemical and structural changes such as morphology control, doping with heteroatoms or ionic systems, or preparation of their nanocomposites. These modifications have effectively addressed the inherent limitations of the above-mentioned photocatalysts and have brought valuable improvement on their photocatalytic performance. Nonetheless, significant input and state-of-the-art ideas are still needed to maximize the use of these metal oxides in a wide range of applications such as the removal of heavy metals, poisonous gas sensing, textile coating for wearable electronic devices, biomedical applications, and the aforementioned photocatalytic degradation of organic contaminants.

Author Contributions: The authors are contributed equally. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kalita, E.; Baruah, J. Environmental remediation. In *Colloidal Metal Oxide Nanoparticles*; Thomas, S., Tresa Sunny, A., Velayudhan, P., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 525–576. ISBN 978-0-12-813357-6.
2. Englande, A.J.; Krenkel, P.; Shamas, J. Wastewater Treatment & Water Reclamation. In *Reference Module in Earth Systems and Environmental Sciences*; Elsevier: Amsterdam, The Netherlands, 2015; ISBN 978-0-12-409548-9.
3. Breitburg, D.; Levin, L.A.; Oschlies, A.; Grégoire, M.; Chavez, F.P.; Conley, D.J.; Garçon, V.; Gilbert, D.; Gutiérrez, D.; Isensee, K.; et al. Declining Oxygen in the Global Ocean and Coastal Waters. *Science* **2018**, *359*, eaam7240. [[CrossRef](#)] [[PubMed](#)]
4. Nguyen, T.T.; Nam, S.N.; Kim, J.; Oh, J. Photocatalytic Degradation of Dissolved Organic Matter under ZnO-Catalyzed Artificial Sunlight Irradiation System. *Sci. Rep.* **2020**, *10*, 13090. [[CrossRef](#)] [[PubMed](#)]
5. Ajmal, A.; Majeed, I.; Malik, R.N.; Idriss, H.; Nadeem, M.A. Principles and Mechanisms of Photocatalytic Dye Degradation on TiO₂ Based Photocatalysts: A Comparative Overview. *RSC Adv.* **2014**, *4*, 37003–37026. [[CrossRef](#)]
6. Zaharia, C.; Suteu, D.; Muresan, A.; Muresan, R.; Popescu, A. Textile Wastewater Treatment by Homogeneous Oxidation with Hydrogen Peroxide. *Environ. Eng. Manag. J.* **2009**, *8*, 1359–1369. [[CrossRef](#)]
7. Gusain, R.; Gupta, K.; Joshi, P.; Khatri, O.P. Adsorptive Removal and Photocatalytic Degradation of Organic Pollutants Using Metal Oxides and their Composites: A Comprehensive Review. *Adv. Colloid Interface Sci.* **2019**, *272*, 102009. [[CrossRef](#)]
8. Carmen, Z.; Daniela, S. Textile Organic Dyes—Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents—A Critical Overview. In *Organic Pollutants Ten Years after the Stockholm Convention—Environmental and Analytical Update*; IntechOpen: London, UK, 2012; pp. 3–86. ISBN 978-953-307-917-2.

9. Hitam, C.N.C.; Jalil, A.A. A Review on Exploration of Fe₂O₃ Photocatalyst towards Degradation of Dyes and Organic Contaminants. *J. Environ. Manag.* **2020**, *258*, 110050. [[CrossRef](#)]
10. Gautam, S.; Agrawal, H.; Thakur, M.; Akbari, A.; Sharda, H.; Kaur, R.; Amini, M. Metal Oxides and Metal Organic Frameworks for the Photocatalytic Degradation: A Review. *J. Environ. Chem. Eng.* **2020**, *8*, 103726. [[CrossRef](#)]
11. Schwanke, A.J.; Balzer, R.; Pergher, S. Microporous and Mesoporous Materials from Natural and Inexpensive Sources. In *Handbook of Ecomaterials*; Martínez, L., Kharissova, O., Kharisov, B., Eds.; Springer: Berlin/Heidelberg, Germany, 2019; pp. 3379–3399. [[CrossRef](#)]
12. Li, R.; Li, T.; Zhou, Q. Impact of Titanium Dioxide (TiO₂) Modification on its Application to Pollution Treatment—A Review. *Catalysts* **2020**, *10*, 804. [[CrossRef](#)]
13. Theerthagiri, J.; Chandrasekaran, S.; Salla, S.; Elakkiya, V.; Senthil, R.A.; Nithyadharseni, P.; Mailayagan, T.; Micheal, K.; Ayeshamarian, A.; Arasu, M.V.; et al. Recent Developments of Metal Oxide Based Heterostructures for Photocatalytic Applications towards Environmental Remediation. *J. Solid State Chem.* **2018**, *267*, 35–52. [[CrossRef](#)]
14. Loddo, V.; Bellardita, M.; Camera-Roda, G.; Parrino, F.; Palmisano, L. Chapter 1 — Heterogeneous Photocatalysis: A Promising Advanced Oxidation Process. In *Current Trends and Future Developments on (Bio-) Membranes*; Basile, A., Mozia, S., Molinari, R., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 1–43. ISBN 978-0-12-813549-5.
15. Curti, M.; Bahnemann, D.W.; Mendive, C.B. Mechanisms in Heterogeneous Photocatalysis: Titania under UV and Visible Light Illumination. In *Reference Module in Materials Science and Materials Engineering*; Elsevier: Amsterdam, The Netherlands, 2016; ISBN 978-0-12-803581-8.
16. Kiriakidis, G.; Binas, V. Metal Oxide Semiconductors as Visible Light Photocatalysts. *J. Korean Phys. Soc.* **2014**, *65*, 297–302. [[CrossRef](#)]
17. Jeevanandam, J.; Barhoum, A.; Chan, Y.S.; Dufresne, A.; Danquah, M.K. Review on Nanoparticles and Nanostructured Materials: History, Sources, Toxicity and Regulations. *Beilstein J. Nanotechnol.* **2018**, *9*, 1050–1074. [[CrossRef](#)] [[PubMed](#)]
18. Khin, M.M.; Nair, A.S.; Babu, V.J. A Review on Nanomaterials for Environmental Remediation. *Energy Environ. Sci.* **2012**, *5*, 8075–8109. [[CrossRef](#)]
19. Rodríguez, J.A.; Fernández-García, M. *Synthesis, Properties, and Applications of Oxide Nanomaterials*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2007.
20. Stankic, S.; Suman, S.; Haque, F.; Vidic, J. Pure and Multi Metal Oxide Nanoparticles: Synthesis, Antibacterial and Cytotoxic Properties. *J. Nanobiotechnology* **2016**, *14*, 1–20. [[CrossRef](#)] [[PubMed](#)]
21. Farahmandjou, M.; Soflaee, F. I Synthesis of Iron Oxide Nanoparticles using Borohydride. *Int. J. Bio-Inorg. Hybr. Nanomater.* **2014**, *3*, 203–206.
22. Zhang, R.; Gao, L. Preparation of Nanosized Titania by Hydrolysis of Alkoxide Titanium in Micelles. *Mater. Res. Bull.* **2002**, *37*, 1659–1666. [[CrossRef](#)]
23. Yu, J.C.; Yu, J.; Ho, W.; Zhang, L. Preparation of Highly Photocatalytic Active Nano-Sized TiO₂ Particles via Ultrasonic Irradiation. *Chem. Commun.* **2001**, *1*, 1942–1943. [[CrossRef](#)]
24. Armelao, L.; Barreca, D.; Bertapelle, M.; Bottaro, G.; Sada, C.; Tondello, E. A Sol-gel Approach to Nanophasic Copper Oxide Thin Films. *Thin Solid Film.* **2003**, *442*, 48–52. [[CrossRef](#)]
25. Singh, J.; Dutta, T.; Kim, K.H.; Rawat, M.; Samddar, P.; Kumar, P. “Green” Synthesis of Metals and Their Oxide Nanoparticles: Applications for Environmental Remediation. *J. Nanobiotechnology* **2018**, *16*, 1–24. [[CrossRef](#)]
26. Akintelu, S.A.; Folorunso, A.S.; Folorunso, F.A.; Oyebamiji, A.K. Green Synthesis of Copper Oxide Nanoparticles for Biomedical Application and Environmental Remediation. *Heliyon* **2020**, *6*, e04508. [[CrossRef](#)]
27. Romain, A.C.; Nicolas, J. Long Term Stability of Metal Oxide-Based Gas Sensors for e-Nose Environmental Applications: An Overview. *Sens. Actuators B Chem.* **2010**, *146*, 502–506. [[CrossRef](#)]
28. Gao, Y.; Pu, X. Combustion Synthesis of Graphene Oxide—TiO₂ Hybrid Materials for Photodegradation of Methyl Orange. *Carbon* **2012**, *50*, 4093–4101. [[CrossRef](#)]
29. Fu, F.; Wang, Q. Removal of Heavy Metal Ions from Wastewaters: A Review. *J. Environ. Manag.* **2011**, *92*, 407–418. [[CrossRef](#)] [[PubMed](#)]
30. Latif, A.; Sheng, D.; Sun, K.; Si, Y.; Azeem, M.; Abbas, A.; Bilal, M. Remediation of Heavy Metals Polluted Environment Using Fe-Based Nanoparticles: Mechanisms, Influencing Factors, and Environmental Implications. *Environ. Pollut.* **2020**, *264*, 114728. [[CrossRef](#)] [[PubMed](#)]
31. Tamar, R.; Ossman, M.E.; Mansou, M.S.; Farag, H.A. Metal Oxide Nano-particles as an Adsorbent for Removal of Heavy Metals. *J. Adv. Chem. Eng.* **2015**, *5*, 1–8. [[CrossRef](#)]
32. Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lu, L.; Zhang, Q. Heavy Metal Removal from Water/Wastewater by Nanosized Metal Oxides: A Review. *J. Hazard. Mater.* **2012**, *212*, 317–331. [[CrossRef](#)]
33. Ronsse, F.; Nachenius, R.W.; Prins, W. Carbonization of Biomass. In *Recent Advances in Thermo-Chemical Conversion of Biomass*; Elsevier B.V.: Amsterdam, The Netherlands.
34. Pandey, A.; Bhaskar, T.; Stöcker, M.; Sukumaran, R.K. (Eds.) *Recent Advances in Thermo-Chemical Conversion of Biomass*; Elsevier: Boston, MA, USA, 2015; pp. 293–324. ISBN 978-0-444-63289-0.
35. Lam, D.V.; Won, S.; Shim, H.C.; Kim, J.H.; Lee, S.M. Turning Cotton into Tough Energy Textile via Metal Oxide Assisted Carbonization. *Carbon* **2019**, *153*, 257–264. [[CrossRef](#)]

36. Zhang, D.; Jin, Y.; Cao, Y. Facile Synthesis and Ammonia Gas Sensing Properties of NiO Nanoparticles Decorated MoS₂ Nanosheets Heterostructure. *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 573–581. [[CrossRef](#)]
37. Kumar, A.; Sanger, A.; Kumar, A.; Chandra, R. Fast Response Ammonia Sensors Based on TiO₂ and NiO Nanostructured Bilayer Thin Films. *RSC Adv.* **2016**, *6*, 77636–77643. [[CrossRef](#)]
38. O'Regan, B.; Gratzel, M. A Low-Cost, High Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films. *Nature* **1991**, *354*, 737–740. [[CrossRef](#)]
39. Wang, G.; Yang, Y.; Han, D.; Li, Y. Oxygen Defective Metal Oxides for Energy Conversion and Storage. *Nano Today* **2017**, *13*, 23–39. [[CrossRef](#)]
40. Cho, J.; Losego, M.D.; Zhang, H.G.; Kim, H.; Zuo, J.; Petrov, I.; Cahill, D.G.; Braun, P.V. Electrochemically Tunable Thermal Conductivity of Lithium Cobalt Oxide. *Nat. Commun.* **2014**, *5*, 1–6. [[CrossRef](#)]
41. Babu, A.T.; Antony, R. Green Synthesis of Silver Doped Nano Metal Oxides of Zinc & Copper for Antibacterial Properties, Adsorption, Catalytic Hydrogenation & Photodegradation of Aromatics. *J. Environ. Chem. Eng.* **2019**, *7*, 102840. [[CrossRef](#)]
42. Pramanik, A.; Datta, A.K.; Das, D.; Kumbhakar, D.V.; Ghosh, B.; Mandal, A.; Gupta, S.; Sengupta, S. Assessment of Nanotoxicity (Cadmium Sulphide and Copper Oxide) Using Cytogenetical Parameters in Coriandrum sativum L. (Apiaceae). *Cytol. Genet.* **2018**, *52*, 299–308. [[CrossRef](#)]
43. Dai, Z.; Yang, A.; Bao, X.; Yang, R. Facile Non-Enzymatic Electrochemical Sensing for Glucose Based on Cu₂O–BSA Nanoparticles Modified GCE. *Sensors* **2019**, *19*, 2824. [[CrossRef](#)] [[PubMed](#)]
44. Malathi, A.; Madhavan, J.; Ashokkumar, M.; Arunachalam, P. A review on BiVO₄ Photocatalyst: Activity Enhancement Methods for Solar Photocatalytic Applications. *Appl. Catal. A Gen.* **2018**, *555*, 47–74. [[CrossRef](#)]
45. Hitam, C.N.C.; Jalil, A.A.; Triwahyono, S.; Rahman, A.F.A.; Hassan, N.S.; Khusnun, N.F.; Jamian, S.F.; Mamat, C.R.; Nabgan, W.; Ahmad, A. Effect of Carbon-Interaction on Structure-Photoactivity of Cu Doped Amorphous TiO₂ Catalysts for Visible-Light-Oriented Oxidative Desulphurization of Dibenzothiophene. *Fuel* **2018**, *216*, 407–417. [[CrossRef](#)]
46. Rahman, A.F.A.; Jalil, A.A.; Triwahyono, S.; Ripin, A.; Aziz, F.F.A.; Fatah, N.A.A.; Jaafar, N.F.; Hitam, C.N.C.; Salleh, N.F.M.; Hassan, N.S. Strategies for Introducing Titania onto Mesostructured Silica Nanoparticles Targeting Enhanced Photocatalytic Activity of Visible-Light-Responsive Ti-MSN Catalysts. *J. Clean Prod.* **2016**, *143*, 1–12. [[CrossRef](#)]
47. Frank, S.N.; Bard, A.J. Heterogeneous Photocatalytic Oxidation of Cyanide and Sulfite in Aqueous Solutions at Semiconductor Powders. *J. Phys. Chem.* **1977**, *81*, 1484–1488. [[CrossRef](#)]
48. Xie, W.; Li, R.; Xu, Q. Enhanced Photocatalytic Activity of Se-Doped TiO₂ under Visible Light Irradiation. *Sci. Rep.* **2018**, *8*, 1–10. [[CrossRef](#)]
49. Miyamoto, N.S.; Miyamoto, R.; Giamello, E.; Kurisaki, T.; Wakita, H. Characterization and Photocatalytic Properties of Lutetium Ion-Doped Titanium Dioxide Photocatalyst. *Res. Chem. Intermed.* **2018**, *44*, 4577–4594. [[CrossRef](#)]
50. Jaafar, N.F.; Jalil, A.A.; Triwahyono, S.; Efendi, J.; Mukti, R.R.; Jusoh, R.; Jusoh, N.W.C.; Karim, A.H.; Salleh, N.F.M.; Suendo, V. Direct in situ Activation of Ag⁰ Nanoparticles in Synthesis of Ag/TiO₂ and its Photoactivity. *Appl. Surf. Sci.* **2015**, *38*, 75–84. [[CrossRef](#)]
51. Shan, R.; Lu, L.; Gu, J.; Zhang, Y.; Yuan, H.; Chen, Y.; Luo, B. Photocatalytic Degradation of Methyl Orange by Ag/TiO₂/Biochar Composite Catalysts in Aqueous Solutions. *Mater. Sci. Semicond. Process.* **2020**, *114*, 105088. [[CrossRef](#)]
52. Harja, M.; Sescu, A.M.; Favier, L.; Lutic, D. Doping Titanium Dioxide with Palladium for Enhancing the Photocatalytic Decontamination and Mineralization of a Refractory Water Pollutant. *Rev. Chim.* **2020**, *71*, 145–152. [[CrossRef](#)]
53. Liu, D.; Wang, J.; Zhou, J.; Xi, Q.; Li, X.; Nie, E.; Piao, X.; Sun, Z. Fabricating I-Doped TiO₂ Photoelectrode for the Degradation of Diclofenac: Performance and Mechanism Study. *Chem. Eng. J.* **2019**, *369*, 968–978. [[CrossRef](#)]
54. Basavarajappa, P.S.; Patil, S.B.; Ganganagappa, N.; Reddy, K.R.; Raghu, A.V.; Reddy, C.V. Recent Progress in Metal-Doped TiO₂, Non-metal Doped/Codoped TiO₂ and TiO₂ Nanostructured Hybrids for Enhanced Photocatalysis. *Int. J. Hydrog. Energy* **2020**, *45*, 7764–7778. [[CrossRef](#)]
55. Xiong, Y.; He, D.; Jaber, R.; Cameron, P.J.; Edler, K.J. Sulfur-Doped Cubic Mesostructured Titania Films for Use as a Solar Photocatalyst. *J. Phys. Chem. C* **2017**, *121*, 9929–9937. [[CrossRef](#)]
56. Wang, M.; Han, J.; Hu, Y.; Guo, R. Enhanced Visible Light Photocatalytic Performance. *RSC Adv.* **2017**, *7*, 15513–15520. [[CrossRef](#)]
57. Zhang, S.; Lu, X. Treatment of Wastewater Containing Reactive Brilliant Blue KN-R using TiO₂/BC Composite as Heterogeneous Photocatalyst and Adsorbent. *Chemosphere* **2018**, *206*, 777–783. [[CrossRef](#)]
58. Liao, F.; Chu, L.; Guo, C.; Guo, Y.; Ke, Q.; Guo, Y. Ytterbium Doped TiO₂ Nanofibers on Activated Carbon Fibers Enhances Adsorption and Photocatalytic Activities for Toluene Removal. *ChemistrySelect* **2019**, *4*, 9222–9231. [[CrossRef](#)]
59. Saqib, N.U.; Adnan, R.; Shah, I. Zeolite Supported TiO₂ with Enhanced Degradation Efficiency for Organic Dye Under Household Compact Fluorescent Light. *Mater. Res. Express* **2019**, *6*, 095506. [[CrossRef](#)]
60. Zhu, P.; Ren, Z.; Wang, R.; Duan, M.; Xie, L.; Xu, J.; Tian, Y. Preparation and Visible Photocatalytic Dye Degradation of Mn-TiO₂/Sepiolite Photocatalysts. *Front. Mater. Sci.* **2020**, *14*, 33–42. [[CrossRef](#)]
61. Ramos, D.K.C.; González, M.V.; Muñoz, R.A.E.; Cruz, J.S.; De Moure-Flores, F.J.; Mayén-Hernández, S.A. Obtaining and Characterization of TiO₂-GO Composites for Photocatalytic Applications. *Int. J. Photoenergy* **2020**, *2020*, 1–9. [[CrossRef](#)]
62. Fu, Z.; Zhang, S.; Fu, Z. Preparation of Multicycle GO/TiO₂ Composite Photocatalyst and Study on Degradation of Methylene Blue Synthetic Wastewater. *Appl. Sci.* **2019**, *9*, 3282. [[CrossRef](#)]

63. Liu, Z.; Tian, J.; Zeng, D.; Yu, C.; Huang, W.; Yang, K.; Liu, X.; Liu, H. Binary-phase TiO₂ Modified Bi₂MoO₆ Crystal for Effective Removal of Antibiotics under Visible Light Illumination. *Mater. Res. Bull.* **2019**, *112*, 336–345. [[CrossRef](#)]
64. Abbas, K.K.; Shabeeb, K.M.; Aljanabi, A.A.A.; Al-Ghaban, A.M.H.A. Photocatalytic Degradation of Cefazolin Over Spherical Nanoparticles of TiO₂/ZSM-5 Mesoporous Nanoheterojunction Under Simulated Solar Light. *Environ. Technol. Innov.* **2020**, *20*, 101070. [[CrossRef](#)]
65. Lee, K.M.; Lai, C.W.; Ngai, K.S.; Juan, J.C. Recent Developments of Zinc Oxide Based Photocatalyst in Water Treatment Technology: A Review. *Water Res.* **2016**, *88*, 428–448. [[CrossRef](#)]
66. Shirdel, B.; Behnajady, M.A. Visible-Light Induced Degradation of Rhodamine B by Ba-doped ZnO Nanoparticles. *J. Mol. Liq.* **2020**, *315*, 113633. [[CrossRef](#)]
67. Ponnamma, D.; Cabibihan, J.; Rajan, M.; Pethaiah, S.S.; Deshmukh, K.; Gogoi, P.J.; Pasha, S.K.K.; Ahamed, M.B.; Krishnegowda, J.; Chandrashekar, B.N.; et al. Synthesis, Optimization and Applications of ZnO/Polymer Nanocomposites. *Mater. Sci. Eng. C* **2019**, *98*, 1210–1240. [[CrossRef](#)]
68. Chen, X.; Wu, Z.; Liu, D.; Gao, Z. Preparation of ZnO Photocatalyst for the Efficient and Rapid Photocatalytic Degradation of Azo Dyes. *Nanoscale Res. Lett.* **2017**, *12*, 4–13. [[CrossRef](#)]
69. Balcha, A.; Yadav, O.P.; Dey, T. Photocatalytic Degradation of Methylene Blue Dye by Zinc Oxide Nanoparticles Obtained From Precipitation and Sol-Gel Methods. *Environ. Sci. Pollut. Res.* **2016**, *23*, 25485–25493. [[CrossRef](#)]
70. Ba-Abbad, M.M.; Kadhum, A.A.H.; Mohamad, A.B.; Takriff, M.S.; Sopian, K. Visible Light Photocatalytic Activity of Fe³⁺-Doped ZnO Nanoparticle Prepared via Sol-Gel Technique. *Chemosphere* **2013**, *91*, 1604–1611. [[CrossRef](#)] [[PubMed](#)]
71. Khan, H.; Habib, M.; Khan, A.; Boffito, D.C. A Modified Sol-Gel Synthesis to Yield a Stable Fe³⁺/ZnO Photocatalyst: Degradation of Water Pollutants and Mechanistic Insights under UV and Visible Light. *J. Environ. Chem. Eng.* **2020**, *8*, 104282. [[CrossRef](#)]
72. Jayakrishnan, A.R.; Alex, K.V.; Tharakan, A.T.; Kamakshi, K.; Silva, J.P.B.; Prasad, M.S.; Sekhar, K.C.; Gomez, M.J.M. Barium-Doped Zinc Oxide Thin Films as Highly Efficient and Reusable Photocatalysts. *ChemistrySelect* **2020**, *5*, 2824–2834. [[CrossRef](#)]
73. Wang, P.; Yang, L.; Li, J.; Sadeh, B. Zn/ZnO Heterostructure for the Application of MO Degradation and NO Removal. *Catal. Lett.* **2020**, *150*, 1985–1992. [[CrossRef](#)]
74. Gu, C.; Xiong, S.; Zhong, Z.; Wang, Y.; Xing, W. A Promising Carbon Fiber-Based Photocatalyst with Hierarchical Structure for Dye Degradation. *RSC Adv.* **2017**, *7*, 22234–22242. [[CrossRef](#)]
75. Beura, R.; Pachaiappan, R.; Paramasivam, T. Photocatalytic Degradation Studies of Organic Dyes over Novel Ag-Loaded ZnO-Graphene Hybrid Nanocomposites. *J. Phys. Chem. Solids* **2021**, *148*, 109689. [[CrossRef](#)]
76. Di Mauro, A.; Farrugia, C.; Abela, S.; Refalo, P.; Grech, M.; Falqui, L.; Privetera, V.; Impellizzeri, G. Synthesis of ZnO/PMMA Nanocomposite by Low-Temperature Atomic Layer Deposition for Possible Photocatalysis Applications. *Mater. Sci. Semicond. Process.* **2020**, *118*, 105214. [[CrossRef](#)]
77. Mugunthan, E.; Saidutta, M.B.; Jagadeeshbabu, P.E. Photocatalytic Activity of ZnO-WO₃ for Diclofenac Degradation under Visible Light Irradiation. *J. Photochem. Photobiol. A Chem.* **2019**, *383*, 111993. [[CrossRef](#)]
78. Sharma, M.; Poddar, M.; Gupta, Y.; Nigam, S.; Avasthi, D.K.; Adelung, R. Solar Light Assisted Degradation of Dyes and Adsorption of Heavy Metal Ions from Water by CuO-ZnO Tetrapodal Hybrid Nanocomposite. *Mater. Today Chem.* **2020**, *17*, 100336. [[CrossRef](#)]
79. Acedo-Mendoza, A.G.; Infantes-Molina, A.; Vargas-Hernández, D.; Chávez-Sánchez, C.A.; Rodríguez-Castellón, E.; Tánori-Córdova, J.C. Photodegradation of Methylene Blue and Methyl Orange with CuO Supported on ZnO Photocatalysts: The Effect of Copper Loading and Reaction Temperature. *Mater. Sci. Semicond. Process.* **2020**, *119*, 105257. [[CrossRef](#)]
80. Dong, P.; Hou, G.; Xi, X.; Shao, R.; Dong, F. WO₃-Based Photocatalysts: Morphology Control, Activity Enhancement and Multifunctional Applications. *Environ. Sci. Nano* **2017**, *4*, 539–557. [[CrossRef](#)]
81. Quan, H.; Gao, Y.; Wang, W. Tungsten Oxide-based Visible Light-Driven Photocatalysts: Crystal and Electronic Structures and Strategies for Photocatalytic Efficiency Enhancement. *Inorg. Chem. Front.* **2020**, *7*, 817–838. [[CrossRef](#)]
82. Janáky, C.; Rajeshwar, K.; Tacconi, N.; Chanmanee, W.; Huda, M. Tungsten-based Oxide Semiconductors for Solar Hydrogen Generation. *Catal. Today* **2013**, *199*, 53–64. [[CrossRef](#)]
83. Dong, P.; Xu, N.; Xu, Y.; Wang, X. A Study of Pt/WO₃-carrier Catalysts for Photocatalytic Purification of NO Gas. *Catal. Commun.* **2016**, *84*, 142–146. [[CrossRef](#)]
84. Mohagheghian, A.; Karimi, S.; Yang, J.; Shirzad-Siboni, M. Photocatalytic Degradation of Diazinon by Illuminated WO₃ Nanopowder. *Desalination Water Treat.* **2016**, *57*, 8262–8269. [[CrossRef](#)]
85. Nguyen, T.; Nam, S.; Son, J.; Oh, J. Tungsten Trioxide (WO₃)-assisted Photocatalytic Degradation of Amoxicillin by Simulated Solar Irradiation. *Sci. Rep.* **2019**, *9*, 9349. [[CrossRef](#)]
86. Govindaraj, T.; Mahendran, C. One-Pot Synthesis of Tungsten Oxide Nanostructured for Enhanced Photocatalytic Organic Dye Degradation. *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 17535–17549. [[CrossRef](#)]
87. Elsayed, E.M.; Elnouby, M.S.; Gouda, M.H.; Elessawy, N.A.; Santos, D.M.F. Effect of the Morphology of Tungsten Oxide Embedded in Sodium Alginate/Polyvinylpyrrolidone Composite Beads on the Photocatalytic Degradation of Methylene Blue Dye Solution. *Materials* **2020**, *13*, 1905. [[CrossRef](#)]
88. Adhikari, S.; Chandra, K.; Kim, D.; Madras, G.; Sarkar, D. Understanding the Morphological Effects of WO₃ Photocatalysts for the Degradation of Organic Pollutants. *Adv. Powder Technol.* **2018**, *29*, 1591–1600. [[CrossRef](#)]

89. Yao, S.; Zhang, X.; Qu, F.; Umar, A.; Wu, X. Hierarchical WO₃ Nanostructures Assembled by Nanosheets and their Applications in Wastewater Purification. *J. Alloys Compd.* **2016**, *689*, 570–574. [[CrossRef](#)]
90. Yao, S.; Qu, F.; Wang, G.; Wu, X. Facile Hydrothermal Synthesis of WO₃ Nanorods for Photocatalysts and Supercapacitors. *J. Alloys Compd.* **2017**, *724*, 695–702. [[CrossRef](#)]
91. Liang, Y.; Yang, Y.; Zou, C.; Xu, K.; Luo, X.; Luo, T.; Li, J.; Yang, Q.; Shi, P.; Yuan, C. 2D Ultra-Thin WO₃ Nanosheets with Dominant {002} Crystal Facets For High-Performance Xylene Sensing and Methyl Orange Photocatalytic Degradation. *J. Alloys Compd.* **2019**, *783*, 848–854. [[CrossRef](#)]
92. Mehmood, F.; Iqbal, J.; Ismail, M.; Mehmood, A. Ni Doped WO₃ Nanoplates: An Excellent Photocatalyst and Novel Nanomaterial for Enhanced Anticancer Activities. *J. Alloys Compd.* **2018**, *746*, 729–738. [[CrossRef](#)]
93. Zhang, J.; Fu, X.; Hao, H.; Gan, W. Facile Synthesis 3D Flower-Like Ag@WO₃ Nanostructures and Applications in Solar-Light Photocatalysis. *J. Alloys Compd.* **2018**, *757*, 134–141. [[CrossRef](#)]
94. Dhanalakshmi, M.; Prabavathi, S.; Saravanakumar, K.; Jones, B.; Muthuraj, V. Iridium Nanoparticles Anchored WO₃ Nanocubes as an Efficient Photocatalyst for Removal of Refractory Contaminants (Crystal Violet and Methylene Blue). *Chem. Phys. Lett.* **2020**, *745*, 137285. [[CrossRef](#)]
95. Sajjad, S.; Khan, M.; Leghari, S.; Ryma, N.; Farooqi, S. Potential Visible WO₃/GO Composite Photocatalyst. *Int. J. Appl. Ceram. Technol.* **2019**, *16*, 1218–1227. [[CrossRef](#)]
96. Smrithi, S.P.; Kottam, N.; Arpitha, V.; Narula, A.; Anikumar, G.N.; Subramanian, K. Tungsten Oxide Modified with Carbon Nanodots: Integrating Adsorptive and Photocatalytic Functionalities for Water Remediation. *J. Sci. Adv. Mater. Devices* **2020**, *5*, 73–83. [[CrossRef](#)]
97. Bang, H.; Huy, B.T.; Kumar, S.; Lee, Y.; Cho, J.; Hur, J. H₂O₂-Assisted Photocatalysis for Removal of Natural Organic Matter using Nanosheet C₃N₄-WO₃ Composite under Visible Light and the Hybrid System with Ultra Filtration. *Chem. Eng. J.* **2020**, *399*, 125733. [[CrossRef](#)]
98. Xie, R.; Fang, K.; Liu, Y.; Chen, W.; Fan, J.; Wang, X.; Ren, Y.; Song, Y. Z-Scheme In₂O₃/WO₃ Heterogeneous Photocatalysts with Enhanced Visible-Light-Driven Photocatalytic Activity toward Degradation of Organic Dyes. *J. Mater. Sci.* **2020**, *26*. [[CrossRef](#)]
99. Czech, B.; Zygmunt, P.; Kadirova, Z.C.; Yubuta, K.; Hojamberdiev, M. Effective Photocatalytic Removal of Selected Pharmaceuticals and Personal Care Products by Elsmoreite/Tungsten Oxide@Zns Photocatalyst. *J. Environ. Manag.* **2020**, *270*, 110870. [[CrossRef](#)]
100. Masudy-Panah, S.; Katal, R.; Khiavi, N.D.; Shekarian, E.; Hu, J.; Gong, X. A High-Performance Cupric Oxide Photocatalyst with Palladium Light Trapping Nanostructures and A Hole Transporting Layer for Photoelectrochemical Hydrogen Evolution. *J. Mater. Chem. A* **2019**, *7*, 22332–22345. [[CrossRef](#)]
101. Sabzehei, K.; Hadavi, S.H.; Bajestani, M.G.; Sheibani, S. Comparative Evaluation of Copper Oxide Nano-Photocatalyst Characteristics by Formation of Composite with TiO₂ and ZnO. *Solid State Sci.* **2020**, *107*, 106362. [[CrossRef](#)]
102. Shah, A.; Sharma, V.K.; Punjabi, P.B. Photodegradation of Two Commercial Dyes in Aqueous Phase Using Copper Oxide as Photocatalyst. *Int. J. Chem. Sci.* **2009**, *7*, 2345–2353.
103. Muthukumar, M.; Dhinakaran, G.; Venkatachalam, K.; Sagadevan, S.; Gunasekaran, S.; Podder, J.; Mohammad, F.; Shhid, M.M.; Oh, W.C. Green Synthesis of Cuprous Oxide Nanoparticles for Environmental Remediation and Enhanced Visible-Light Photocatalytic Activity. *Optik* **2020**, *214*, 164849. [[CrossRef](#)]
104. Prado-Chay, D.A.; Cortés-Jácome, M.A.; Angeles-Chávez, C.; Oviedo-Roa, R.; Martínez-Magadán, J.M.; Zuriaga-Monroy, C.; Hernández-Hernández, I.J.; Mayoral, P.R.; Gómora-Herrera, D.R.; Toledo-Antonio, J.A. Synthesis and Photocatalytic Activity of Cu₂O Microspheres upon Methyl Orange Degradation. *Top. Catal.* **2020**, *63*, 586–600. [[CrossRef](#)]
105. Polat, K. Cuprous Oxide Film Sputtered on Monolayer Graphene for Visible Light Sensitive Heterogeneous Photocatalysis. *Thin Solid Film.* **2020**, *709*, 138254. [[CrossRef](#)]
106. Karthikeyan, S.; Ahmed, K.; Osatiashiani, A.; Lee, A.F.; Wilson, K.; Sasaki, K.; Coulson, B.; Swansborough-Aston, W.; Douthwaite, R.E.; Li, W. Pompon Dahlia-like Cu₂O/rGO Nanostructures for Visible Light Photocatalytic H₂ Production and 4-Chlorophenol Degradation. *ChemCatChem* **2020**, *12*, 1699–1709. [[CrossRef](#)]
107. Su, R.; Ge, S.; Li, H.; Su, Y.; Li, Q.; Zhou, W.; Gao, B.; Yue, Q. Science of the Total Environment Synchronous Synthesis of Cu₂O/Cu/Rgo @ Carbon Nanomaterials Photocatalysts via the Sodium Alginate Hydrogel Template Method For Visible Light Photocatalytic Degradation. *Sci. Total Environ.* **2019**, *693*, 133657. [[CrossRef](#)]
108. Shen, H.; Liu, G.; Zhao, Y.; Li, D.; Jiang, J.; Ding, J.; Mao, B.; Shen, H.; Kim, K.-S.; Shi, W. Artificial all-solid-state system by RGO bridged Cu₂O and Bi₂WO₆ for Z-scheme H₂ production and tetracycline degradation. *Fuel* **2020**, *259*, 116311. [[CrossRef](#)]
109. Chen, K.; Wang, X.; Xia, P.; Xie, J.; Wang, J. Efficient Removal of 2,2',4,4'-Tetrabromodiphenyl Ether with a Z-scheme Cu₂O-(rGO-TiO₂) Photocatalyst under Sunlight Irradiation. *Chemosphere* **2020**, *254*, 126806. [[CrossRef](#)]
110. Vaidehi, D.; Bhuvaneshwari, V.; Bharathi, D.; Sheetal, B.P. Antibacterial and Photocatalytic Activity of Copper Oxide Nanoparticles Synthesized Using Solanum Lycopersicum Leaf Extract. *Mater. Res. Express* **2018**, *5*, 085403. [[CrossRef](#)]
111. Rao, M.P.C.; Kulandaivelu, K.; Ponnusamy, V.K.; Wu, J.J.; Sambandam, A. Surfactant-Assisted Synthesis of Copper Oxide Nanorods for the Enhanced Photocatalytic Degradation of Reactive Black 5 Dye In Wastewater. *Environ. Sci. Pollut. Res.* **2020**, *27*, 17438–17445. [[CrossRef](#)] [[PubMed](#)]

112. Sharma, K.; Raizada, P.; Hosseini-Bandegharai, A.; Thakur, P. Fabrication of Efficient CuO/Graphitic Carbon Nitride Based Heterogeneous Photo-Fenton Like Catalyst for Degradation of 2,4-Dimethyl Phenol. *Process Saf. Environ. Prot.* **2020**, *142*, 63–75. [[CrossRef](#)]
113. Ganesan, K.; Jothi, V.K.; Natarajan, A.; Rajaram, A.; Ravichandran, S.; Ramalingam, S. Green Synthesis of Copper Oxide Nanoparticles Decorated with Graphene Oxide for Anticancer Activity and Catalytic Applications. *Arab. J. Chem.* **2020**, *13*, 6802–6814. [[CrossRef](#)]
114. Lu, D.; Zelekew, O.A.; Abay, A.K.; Huang, Q.; Chen, X.; Zheng, Y. Synthesis and Photocatalytic Activities of a CuO/TiO₂ Composite Catalyst Using Aquatic Plants with Accumulated Copper as a Template. *RSC Adv.* **2019**, *9*, 2018–2025. [[CrossRef](#)]
115. Kukovecz, Á.; Kordás, K.; Kiss, J.; Kónya, Z. Atomic Scale Characterization and Surface Chemistry of Metal Modified Titanate Nanotubes and Nanowires. *Surf. Sci. Rep.* **2016**, *71*, 473–546. [[CrossRef](#)]
116. Henderson, M.A. A Surface Science Perspective on TiO₂ Photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185–297. [[CrossRef](#)]
117. László, B.; Baán, K.; Oszkó, A.; Erdőhelyi, A.; Kiss, J.; Kónya, Z. Hydrogen Evolution in the Photocatalytic Reaction between Methane and Water in the Presence of CO₂ on Titanate and Titania Supported Rh and Au Catalysts. *Top. Catal.* **2018**, *61*, 875–888. [[CrossRef](#)]
118. Kiss, J.; Kukovecz, Á.; Kónya, Z. Beyond Nanoparticles: The Role of Sub-Nanosized Metal Species in Heterogeneous Catalysis. *Catal. Lett.* **2019**, *149*, 1441–1454. [[CrossRef](#)]