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Photocatalytic Degradation of Plastic Waste: Recent Progress and Future Perspectives

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Abstract

Microplastics are persistent anthropogenic pollutants that have become a global concern due to their widespread distribution and unfamiliar threat to the environment and living organisms. Conventional technologies are unable to fully decompose and mineralize plastic waste. Therefore, there is a need to develop an environmentally friendly, innovative and sustainable photocatalytic process that can destroy these wastes with much less energy and chemical consumption. In photocatalysis, various nanomaterials based on wide energy band gap semiconductors such as TiO_2 and ZnO are used for the conversion of plastic contaminants into environmentally friendly compounds. In this work, the removal of plastic fragments by photocatalytic reactions using newly developed photocatalytic composites and the mechanism of photocatalytic degradation of microplastics are systematically investigated. In these degradation processes, sunlight or an artificial light source is used to activate the photocatalyst in the presence of oxygen.

Keywords

Plastic Waste, Microplastics, Photocatalytic Method, Degradation, Semiconductors, Heterogeneous Photocatalysts

1. Introduction

Plastic is an indispensable part of the modern lifestyle. Over time, it has supplanted glass, wood, and metal in a variety of things used by humans, such as electronics, medical equipment, ordinary home supplies, and packaging [1]. At this consumption rate, it is estimated that by 2050, up to 33 billion tonnes of plastic will accumulate worldwide [2].

It has been recorded 24.4 trillion pieces of microplastics in the world's oceans

[3]. Microplastic waste is divided into primary plastic as material for products and secondary plastic as miniaturized plastic that is created after the use of plastic. Most of the plastic that flows down the river into the ocean is less dense than water, and this plastic floats along the surface of the sea. However, it sinks to the bottom of the sea due to marine biofouling. An additional problem is that plastic in the ocean can contain carcinogenic polychlorinated biphenyls and polycyclic aromatic hydrocarbons that concentrate marine species [4].

Plastic fragments are often classified by size, with macroplastics being the largest size of 5 mm, followed by microplastics (MP) below 5 mm and nanoplastics (NP) from 1 nm to 1 μm [5]. Microplastics and nanoplastics are suitable for sorption of hazardous pollutants (e.g., persistent chemicals, metal ions) due to their small size, large specific surface area (SSA), and potential to pass into and accumulate in the bodies of organisms [6].

The most common plastics used worldwide include polyethylene (PE), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC), and most of them are difficult to recycle. Linear low-density polyethylene (LLDPE) is widely used in packaging, while polylactic acid (PLA) usually replaces conventional plastics. HDPE has better barrier properties than LDPE and higher stiffness, and is used for blow-moulded bottles for milk and other beverages, and for food containers [7].

According to the British Plastic Federation (BPF) [8], PVC is used extensively in construction, transport, packaging, electrical/electronics and healthcare.

PVC is used for window frames, drainage pipes, water pipes, medical devices, blood bags, cable and wire insulation, resilient flooring, roofing membranes, stationary applications, vehicle interiors and seat covers, fashion and footwear, packaging, cling film, credit cards, records, artificial leather, and other coated fabrics.

Polyethylene (PE) poses a global environmental problem for plastic waste due to its chemical stability and biodegradability. Due to the unique properties of plastics such as lightness, price and durability, plastic is used in various industries such as food industry (food packaging), pharmaceutical industry, chemical industry, etc. Thus, for example, the textile industry, which is not given much attention, will produce about 92 million tons of polymer waste in 2023, with a tendency to increase to about 134 million tons by 2030, from which microplastics can be generated [9].

The compound annual growth rate (CAGR) for the plastics market is estimated to be 4% during the forecast period from 2023 to 2033 [10].

To assess the amount of microplastics in the oceans, marine life, and coastal habitats, numerous studies are being conducted. Thus, in their research, Wu *et al.* found the presence of microplastics in 37.6% of commercial fish from marine farming in the Ma'an archipelago. The fiber was responsible for 90.74% of the microplastics discovered. In the digestive systems of the fish examined, the average abundance of microplastics was 0.43 ± 0.69 items/individual. Furthermore,

cellulose and cellophane were the most prevalent kinds of microplastics found [11].

1.1. The Global Plastics Production

According to the report "Global plastics production 1950-2021" published by Statista Research in 2023, global plastics production in 2021 is estimated at 390.7 million tonnes, an annual increase of 4% [12]. However, according to the latest Plastics Europe 2022 report, China's share of global plastics production continues to increase (to 32% in 2021), while Europe's share—at 57.2 million tonnes in 2021—continues to decline (to 15%). These data are a consequence of the energy crisis caused by the war in Ukraine and the economic crisis during the pandemic COVID. The European plastics industry is investing huge amounts of investment, time, energy, imagination and expertise to sustainably achieve the net zero and circular economy targets for 2050. They are trying to restructure their production and technology base. They are looking for ways to solve problems such as plastic waste and climate change. According to data from Conversio Market & Strategy GmbH and nova Institute, included in the Plastics Europe 2022 report, global production of fossil-based plastics will increase from 332 million tonnes in 2018 to 352.3 million tonnes in 2021. Post-consumer recycled plastics increased from 30 to 32.5 million tonnes and bio-based plastics from 3.5 to 5.9 million tonnes in the same years (**Figure 1**) [13].

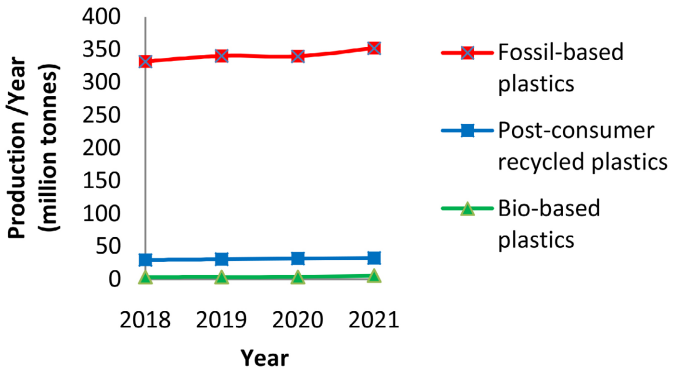

Figure 1. World plastics production.

Plastic is one of the fastest growing pollutants, increasing daily and causing social, environmental and economic concerns. However, the problem with the excessive use of plastics is the generation and treatment of waste and, in particular, the long-term process of degradation and fragmentation of plastics that leads to the creation of micro- and nanoplastics [14]. In addition, micro- and nanoplastics can act as carriers for persistent organic pollutants (POPs), leading to complications for the environment and human health [15]. The presence of microplastics and nanoplastics in the environment poses a significant risk to living organisms (microorganisms, humans, animals and plants) [16]. Therefore, it is extremely important to reduce the use and consumption of plastics and improve

waste management, but it is also strongly recommended to develop policies that regulate the use of plastics and propose recycling and reprocessing measures [17]. Artificial plastic waste in the oceans, seas, rivers, and sediments poses a serious threat to all living organisms on Earth [18] [19].

Plastic additives are chemicals incorporated into plastics from which they can be dissolved out, since most of them are not chemically bound. As a result of the accumulation and fragmentation of plastics in the oceans, plastic additives may pose an increasing ecotoxicological risk to marine organisms [20]. Unfortunately, the composition and toxicological effects of many additives are largely unknown [21].

In this review, the results of the degradation efficiency of macro- and microplastics with previously synthesized photocatalytic materials based on modified titanium dioxide (TiO_2) and zinc oxide (ZnO) are presented. Nevertheless, the existing knowledge on the application of TiO_2 for macro- and microplastics is still limited [22].

1.2. Methods of Plastic Waste Disposal

Disposal and incineration of non-biodegradable plastic waste is a common but inefficient method of waste treatment. For this reason, more and more advanced technologies are being studied and developed. Technologies for processing non-biodegradable plastic waste are divided into recycling (physical recycling, energy recovery and resource recovery) and degradation (biodegradation and oxo-biodegradation). Oxo-biodegradation includes photodegradation, thermal degradation and mechanical-chemical degradation [23].

To reduce the negative impact on the environment, it is necessary to produce plastics that can self-degrade in the future and develop new methods for good recycling of this organic carbon source [24]. Su *et al.* pointed out the importance of photocatalytic conversion of plastic waste into low carbon number products (Cn products, $n \leq 8$) under mild conditions [25]. One of the technologies to improve the degradability of non-degradable plastics is a mixture of polymers and photocatalysts called photocatalytic degradable plastics (PDP).

1.3. Different Methods for Separation and Degradation of MP/NP

Separation and degradation processes are used in the treatment of MP/NP in urban water bodies. During the separation process, the size and chemical composition of MP/NP does not change. Different techniques such as adsorption, coagulation/flocculation, flotation, filtration and magnetic separation are used for its separation [26]. Which of the extraction techniques is used depends on the physicochemical properties of MP/NP such as hydrophilicity, size, shape and magnetic properties. Different functionalized materials (adsorbents) are used for adsorption processes. Thus, magnetic separation is used to separate plastically magnetized nano-Fe_3O_4 from water [27]. Usually, two or more of the above techniques are used to increase the separation efficiency. In many water treatment plants (WTPs), coagulation, flocculation, sedimentation and filtration are

used for MP/NP separation [28]. The degradation process involves the decomposition of MP/NP into less/non-hazardous small-molecule compounds (CO_2 and H_2O) by various methods. To achieve high efficiency of photocatalytic degradation, it is crucial to study the optimal reaction parameters such as temperature, irradiation time (reaction time) and choice of photocatalyst. Disadvantages of combustion, thermal or catalytic decomposition techniques are the release of highly toxic by-products in combustion and high cost and high temperature in thermal conversion and selective catalysts in catalytic conversion. To overcome the existing shortcomings, new technologies such as photocatalytic, especially photochemical decomposition of plastic waste in the solid phase under the temperature and pressure conditions of the environment using solar radiation as a renewable energy source have been studied.

2. Photocatalytic Degradation

Photocatalytic degradation of plastic waste significantly accelerates the degradation rate in the presence of photocatalysts under sunlight. UV radiation is known as the most damaging source to polymers owing to its high energy. Photodegradation of polymers would imply a change in the physical and chemical structure of the polymer as a building block of plastic waste under UV radiation and in the presence of oxygen, that is, chain scission, molecular weight reduction, and molecular shape change occur [29].

The application of heterogeneous photocatalysis for the treatment of water loaded with micro- and nanoplastics is complex process, but it is effective for removing MPs present in water and has already reached the industrial pilot stage. Factors that affect the efficiency of the photocatalytic process of microplastic degradation are microplastic properties (size, shape, and chemical composition), properties and amount of photocatalyst, light source, and surrounding conditions.

2.1. The Mechanisms of Photodegradation of Polymers

Under the influence of solar radiation, microplastics undergo a series of chemical reactions, during which their degradation occurs [30]. Absorption of photons of light causes macromolecules to enter an excited state and causes chain breaking, and branched cross-linking and oxidation reactions occur [31]. In the presence of a photocatalyst, this photodegradation process is even more accelerated.

There are two photodegradation mechanisms of polymers: 1) singlet oxygen mechanism of oxidation, and 2) free radical mechanism of oxidation.

The first mechanism involves the formation of singlet oxygen ($^1O_2$) due to the quenching of the excited triplet state of the corresponding sensitizers (^3S). Further, singlet oxygen can react with the polymer in two ways: 1) oxidizes a vinyl group (-CH=CH_2) and 2) oxidizes an olefin group to form the hydroperoxide functional group (ROOH), respectively. In other words, singlet oxygen could react with the product of the photochemical reaction of ketone and aldehyde, *i.e.* the Norrish reaction (**Figure 2**).

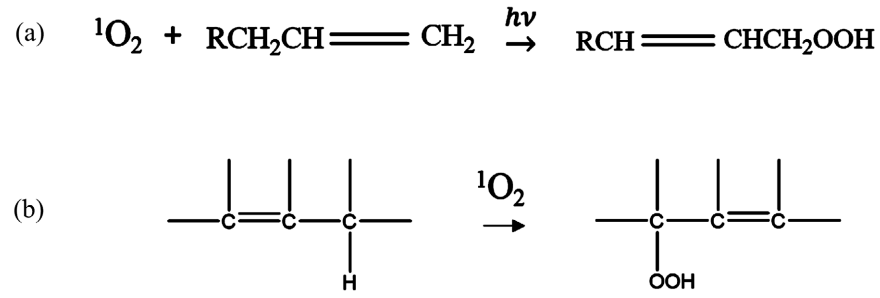

Figure 2. Singlet oxygen mechanism of oxidation of a vinyl group to the hydroperoxide functional group (ROOH) (a) and singlet oxygen mechanism of oxidation of an olefin group to the hydroperoxide functional group (ROOH).

$$^3S + {}^3O_2 \rightarrow {}^1S + {}^1O_2 \quad (1)$$

The second mechanism involves the creation of free radicals by UV radiation which breaks C-C and C-H bonds in polymers. Generated free radicals further react with the oxygen to create the hydroxyl group (O-H) and carbonyl group (C=O) through initiation, propagation, and termination steps.

The initiation step involves the creation of free radicals. A polymer containing an unsaturated chromophore group in its polymer structure (photo-initiator) absorbs light, the polymer chain broken, and hydrogen radicals and polymer radicals are produced (Path 1) [32]. Polymers that do not have an unsaturated chromophore group in their structure, have impurities or structural defects as well as carbonyl groups within the backbone of the polymer that act as photo-initiators [33]. The initiation step can be initiated either by physical or chemical factors. Physical initiation refers to the use of UV radiation and photolytic cleavage of C-C or C-H bonds, while chemical initiation implies the use of catalysts, peroxides or carbonyl groups on unsaturated sites [34].

In the *propagation step* [32] [35] polymer macroradicals react with the O_2 to form polymer peroxyl radicals (·PP) (Path 2). Then, they react with another polymer to produce hydroperoxides and polymer macroradicals (Path 3). Then, the formation of (·PP) occurred by auto-oxidation of polymer macro radicals (Path 4). Subsequently, the two hydroperoxides (HP) react to form polymer alkoxy radicals, polymer peroxide radicals, and H_2O (Path 5). Moreover, the photodecomposition of (HP) leads to the formation of polymer alkoxy radicals and hydroxyl radicals (·OH) (Path 6). Propagation finally leads to chain scission and the formation of olefins and ketones (Path 7). The (·OH) produced will extract hydrogen from another polymer to form polymer macroradicals and H_2O (Path 8).

Further oxidation stimulates chain scission by generating low-molecular-weight oxygenated compounds like hydroxyl, peroxide, and carbonyl groups leading to micro-cracks within the polymeric surface.

In the termination step [32], the formation of inert products occurs by the reaction of free radicals with each other to undergo the crosslinking reaction (Path 9). Inert products and oxygen are formed by the reaction of polymer pe-

roxyl radicals between themselves at high oxygen pressure (Path 10). Conversely, polymeric peroxyl radicals react with polymeric macro radicals at insufficient oxygen pressure (Path 11). In the *termination reaction*, the expected products are olefins and ketones [35]. The entire process of photodegradation of polymers leads to a decrease in their molecular weight, whereby they become more brittle.

2.2. Photocatalytic Degradation Mechanism by Semiconductor Metal Oxides

Tunable physiochemical characteristics of semiconductor metal oxides make them extraordinary as photocatalysts that are capable of providing a sustainable and clean ecosystem.

Zinc oxide (ZnO) is a semiconductor that has high thermal conductivity, high electron mobility, and a wide band gap, 3.2 - 3.4 eV (function only in the UV range) [36]. ZnO due to its low price, high redox potential, nontoxicity, and environmentally friendly features is used as a photocatalyst for the degradation of microplastics. Doping is an excellent method to overcome issues of surface oxygen vacancy and a higher recombination rate of photo-generated charge carriers [37].

Titanium dioxide (TiO_2) is one of the metal oxides wide band gap (3.2 eV) and low conductivity, but after some modifications in composition (doping of other metals, combination with polymers, carbon nanomaterials, formation of heterojunctions with other metal oxides) can be effectively employed as a photocatalyst in the abatement of aqueous pollution. The catalytic performance of titanium dioxide depends on several parameters its crystallinity, surface area, and morphology [38].

The photocatalytic mechanism starts when a photon (hν) with enough energy (equal or higher than the band gap energy, $E \geq E_g$), of the semiconductor achieved its surface. Conduction electrons, e^-, are promoted from the valence band into the conduction band, leaving a hole, h^+, behind. The lifetime of generated electron-hole pairs is only a few nano-seconds, but it is long enough to initiate redox reactions with semiconductor material in aqueous or gaseous phases. The resulting e^--h^+ pairs participate in the oxidation and reduction reactions of the organic compounds. They also may undergo to the recombination process and decrease the quantum yield of the reaction. The hole can either oxidize a compound directly or react with electron donors like water to form ·OH radicals, which in turn react with pollutants such as monomers, polymers and other organic compounds resulting in the total mineralization of most of these compounds [39] [40]. The electrons in the conduction band can react with oxygen, O_2 to yield super oxide anion, then in reaction with water can form hydrogen peroxide (H_2O_2) primary oxygen radical ($\cdot O_2^-$) and then give a hydroxyl radical, (·OH) (**Figure 3**). The resulting (·OH) radicals are non-selective and very strong oxidizing agents (standard redox potential +2.8 V) which leads to complete mineralization, to CO_2 and H_2O of the most of the organic molecules present in wastewater by oxidation reaction. The generation of reactive oxygen species

(ROS) plays an important role in the photocatalytic degradation of (micro)plastics, and superoxide radical ions ($\cdot O_2^-$) and hydroxyl radicals (·OH) participate in the photocatalytic degradation, leading to the polymer chain scission and the production of some intermediates.

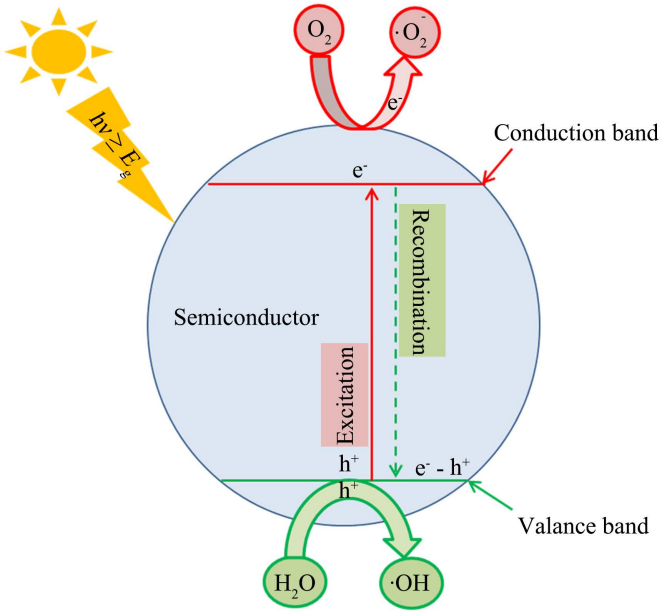

Figure 3. Photocatalytic activity of semiconductor.

3. Recent Achievements in Photocatalytic Degradation of Various Types of Plastic Polymers

There are claims that most photocatalytic degradation technologies investigated to date cannot realize the complete mineralization of (micro)plastics [41]. On the contrary, Nabi *et al.* [42] have developed TiO_2 nanoparticle films with Triton X-100 for photocatalytic degradation of polystyrene (PS) microspheres and polyethylene (PE) under UV light irradiation (**Figure 4**).

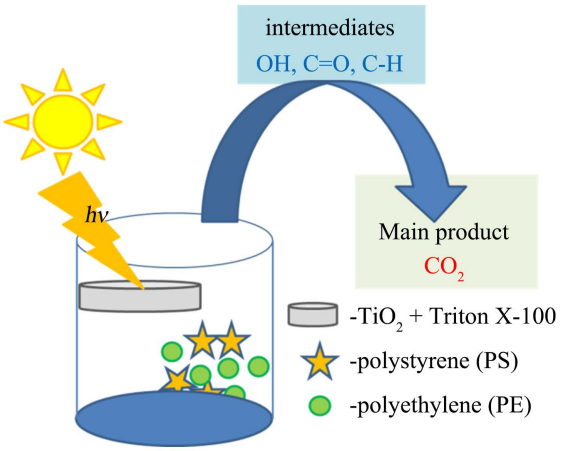

Figure 4. Photocatalytic degradation of polystyrene (PS) microspheres and polyethylene (PE) under UV light irradiation.

Their results have shown complete mineralization (98.40%) of 400-nm PS in 12 h, while degradation of PE presented a high photodegradation rate after 36 h. During photodegradation of PS, carbon dioxide was found as the main end product, while hydroxyl, carbonyl, and carbon-hydrogen groups occurred as intermediates.

Yuwendi *et al.* 2022 [43] synthesized photocatalysts based on Fe- and Ag-modified TiO_2 nanotubes for degradation of polyethylene microplastics. Anodized TiO_2 nanotubes with a voltage of 30 V exhibit the best microplastic degradation results with 17.33% microplastic weight loss in 90 min inside a photoreactor with UVC illumination.

Table 1 summarizes recently developed photocatalysts degradation of plastic waste.

Table 1. List of recently prepared photocatalytic materials for degradation of plastic waste.

Photocatalyst	Plastic material	Degradation results	Light source	Time of irradiation/ temperature	Ref.
Ag-TiO_2 nanotubes	PE-microplastics	−17.33% WL*	UV-C	90 min	[43]
HA-ZnO** HASS-ZnO***	PLA LLDPE		UV-A	75 h 225 h 25˚C	[44]
ZnO	PP 100 mm^2 25 mm^2	−7.8% WL*	UV-C 11 Watt 254 nm	35˚C - 50˚C	[45]
ZnO NR**** + glass fiber	PP	−65% PV*****	Vis		[46]
ZnO-PVP	PE PS	Changes of surface texture	Sun		[47]
F-TiO_2	PE-films PE raw PE composites	−0% WL* −26% WL*	UV-A (LED)	3 weeks	[48]
TiO_2 NP	PE	−56% WL*	UV	504 h	[49]

*WL: Weight Loss, **HA: Humic Acid, ***HASS: Humic Acid Sodium Salt, ****NR: Nano Rods, *****PV: Particle Volume, ******NP: Nano Powder.

3.1. Recently Developed ZnO Heterogeneous Photocatalysts for the Treatment of Plastic Contaminants

3.1.1. Photocatalytic Degradation of LLDPE

Photocatalytic methods are promising eco-friendly and low-cost process for the plastics degradation. Amato *et al.* [44] synthesized an organo-inorganic material containing organic molecule (humic acid) and an inorganic semiconductor (ZnO) which form ligand-to-metal charge transfer complexes (LMCTCs). Herein, ZnO nanoparticles were doped at molecular scale with small percentages of a

commercial humic acid (HA) at low molecular weight and its sodium salt (HASS) was chosen as bio-derived Humic Acids (HAs) leading to hybrid HASS/ZnO and HA/ZnO nanoparticles of about 150 nm. Obtained hybrid humic acids-doped/ZnO nanoparticles (HAs/ZnO) were used as photocatalysts for the degradation of LLDPE and PLA thin films, under UVA/light irradiation. For the photocatalytic reaction, ZnO-based photocatalytic material was coated with polymeric LLDPE and biopolymeric PLA films (4 × 2 cm) and placed in a bath containing water under the UVA/light irradiation (a high-pressure Hg vapour lamp, 125 W) for 75 h and 225 h at 25˚C. Obtained hybrid nanoparticles have shown an enhanced ability to produce ·OH radicals after UVA/light irradiation in aqueous environment probably due to the intrinsic free-radicals of HAs which contribute to the degradation of polyolefin LLDPE and biodegradable PLA films. In particular, HASS/ZnO nanoparticles showed an improved photocatalytic activity compared to bare ZnO for LLDPE film, while HA/ZnO was more effective for the PLA degradation. Significant changes in the polymeric films in terms of the surface properties (the presence of functional groups such as hydroxyl, carbonyl, and carbon-hydrogen) as well as structural and morphological features were observed. They concluded that the presence of bioderived organic components even at low concentration significantly promoted the photo-oxidation thus acting as erosion initiators toward the surface of the polymeric films.

3.1.2. Photocatalytic Degradation of PP

Razali *et al.* (2020) used 1 - 3 g of ZnO nanoparticles (<50 nm) for the photocatalytic degradation of polypropylene (PP) macroplastics (100 mm^2) and microplastics (25 mm^2) in an aqueous environment using batch-slurry photoreactor equipped with an air pump (1.6 L/min) for 6 hours irradiation at 254 nm with an UV-C lamp of 11 watts. A water bath was used to maintain the reaction temperature of 35˚C or 50˚C. Time and temperature were chosen to simulate most solar thermal collectors. The best result that was achieved was 7.8 wt% of plastic weight loss with the 1 g/L ZnO and PP microplastic at 50˚C [45].

Uheida *et al.* 2020 [46] used zinc oxide nanorods (ZnO NRs) immobilized onto glass fibers substrates for photocatalytic degradation of PP microplastics under visible light. They were able to reduce average particle volume by 65%. Furthermore, they identified nontoxic by-products during the photodegradation process.

Lam *et al.* (2022) [47] prepared ZnO-modified polyvinylpyrrolidone (ZnO-PVP) for the photocatalytic degradation of polyethylene (PE) and polystyrene (PS) under direct sunlight. They found that incorporation of PVP can effectively reduce the particle size and prolong the optical response range in the solar spectrum. The interaction between ZnO-PVP and plastic film of PE and PS was improved due to the high surface area of the composite. They explained the changes in the surface texture of the polymer films over ZnO-PVP under sunlight irradiation with the formation of carbonyl, peroxides and vinyl unsaturated groups. In accordance with the experimental data they proposed the mechanism

of the photocatalytic degradation of plastics that include the formation of the holes and hydroxyl radicals.

3.2. Recently Developed TiO_2 Heterogeneous Photocatalysts for the Degradation of Plastic Contaminants

3.2.1. Photocatalytic Degradation of PE

Díez *et al.* successfully synthesized fluoride-doped-TiO_2 and used it for solid-phase photodegradation of polyethylene films [48]. They were able to degrade almost half weight of polyethylene, containing only 2% of the photocatalyst, after three weeks of UVA radiation using a low consumption light emitting diode (LED) lamp. The results have shown that raw PE and PE composite with well-known TiO_2 reduced 0% and 26% of weight after 3 weeks of degradation.

Raj *et al.* exposed ultrasonicated polyethylene (PE) pieces along with TiO_2 nano powder (NP) to UV light. They found 56% weight loss after 504 h of UV irradiation which was accompanied by formation of cavities due to photocatalytic degradation. They observed from FTIR analysis, the change in PE surface when was in contact with ultrasonicated TiO_2 NP, while no change in surface chemistry for samples without TiO_2 NP [49].

Li *et al.* (2010) prepared polypyrrole/TiO_2 (PPy/TiO_2) nanocomposite and used it for the photocatalytic degradation of polyethylene (PE) coming from one-off plastic bag under sunlight. The nanocomposite was prepared by sol-gel and emulsion polymerization methods. They studied and compared the photocatalytic activity of pure TiO_2, PPy and PPy/TiO_2 in degradation of PE. New PE plastic bag was scissored off on the pieces of 6 - 8 cm and put in a culture dish. Prepared nanocomposite (PPy/TiO_2) was weighed to 10% of plastic sample and was spread around uniformly two sides of PE plastic. Experiment started after its exposition to sunlight under the ambient conditions for 6 hours every sunny day and the experimentation was continued for 240 h. The photocatalytic degradations of PE plastic with pure TiO_2 and PPy were also investigated and compared with that of PPy/TiO_2. No noticeable photoinduced weight loss of PE plastic samples when no catalyst and with TiO_2 were employed as photocatalyst under sunlight irradiation, whereas Ppy/TiO_2 exhibits much higher, respectively. For example, weight loss for Ppy/TiO_2 versus Ppy and TiO_2 was 35.4%: 11.7%: 3.2% at 240 h. Therefore, Ppy/TiO_2 nanocomposite shows highly enhanced photodegradation [50].

The solid-phase photocatalytic degradation of polyethylene (PE) plastic with TiO_2 has been investigated by Zhao *et al.* (2007) [51]. They found that PE-TiO_2 composite plastic can be efficiently mineralized until CO_2 and water as the main products. The weight of 42% under solar irradiation for 300 h was achieved for the PE-TiO_2 (1 wt%) film. They explained that the initial degradation of composite plastic starts on PE-TiO_2 interface and then by the diffusion of the reactive oxygen species generated on TiO_2 particle surface extended into polymer matrix.

For the photocatalytic degradation of PE, Zhao *et al.* (2008) synthesized various photocatalysts such as copper phthalocyanine (CuPc) modified TiO_2 (TiO_2/CuPc).

The CuPc promoted charge separation of TiO_2 and enhanced the photocatalytic degradation of PE. Also, in this photodegradation process generation of the reactive oxygen species on TiO_2 or TiO_2/CuPc particle surfaces play important roles. Their research showed that the thin film composed of polymer plastic with TiO_2/CuPc composite photocatalyst is a suitable way to photodegrade plastic contaminants under solar light irradiation [52].

3.2.2. Photocatalytic Degradation of LDPE

Wang *et al.* (2022) studied photocatalytic degradation performance and mechanism of low-density polyethylene (LDPE) containing TiO_2 (LDPE-TiO_2) in water without NaCl, water with NaCl, and air [53]. They found that after two hours of irradiation the total reduction of LDPE-TiO_2 mass was close to 70% for each phase condition. The difference was in lower carbonyl index and lower molecular weight in water compared to air. The formation of organochlorine substance containing C-Cl bond in the debris of LDPE-TiO_2 comes from the presence of chloride ions (Cl^-) and hydroxyl radicals (·OH) in water. For the LDPE-TiO_2 film degradation in the air, the photogenerated electron (e^-) was responsible, while in the water recombination of *electron* with hole occurred.

Kaewkam *et al.* 2022 [54] have done degradation of low-density polyethylene films (LDPE films) with TiO_2 prepared *via* sol-gel method and calcined at two different temperatures (450˚C and 900˚C). They found weight loss (WL) = 17.30% and carbonyl index (CI) = 4.0754 with the use of TiO_2-900˚C along with UV-C light.

Olajire and Mohammed (2021) [55] prepared gold nanoparticles (Au NPs) via the reduction of hydrogen tetrachloroaurate (III) ($HAuCl_4{\cdot}3H_2O$) solution by the aqueous leaf extract of *Ananas comosus*. The photocatalytic activity of prepared AuNPs was studied in degradation of low-density polyethylene (LDPE) film. The LDPE film with 1.0% Au NPs that is the LDPE@Au (1.0 wt%) nanocomposite film showed 6 times higher photoinduced degradation efficiency in 240 h under solar light irradiation than the pure LDPE film. However, LDPE@Au (1.0 wt%) nanocomposite film showed a certain weight loss at the end of 240 h even under the dark condition. Thus, LDPE@Au (1.0 wt%) results in a total degradation efficiency of 90.8% under solar irradiation after 240 h.

3.2.3. Photocatalytic Degradation of HDPE

Ariza-Tarazona *et al.*, 2020 [56] demonstrated that there is a combined effect of pH and temperature in the photocatalysis of HDPE MPs. They reported high HDPE MP photocatalytic degradation efficiency of 70% within 50 h, using the C, N-TiO_2 catalyst in an acidic medium (pH = 3) and at low temperature (273 K).

3.3. Other Semiconductors Used for Photocatalytic Degradation of Plastics

3.3.1. Photocatalytic Degradation of PS

Acuña-Bedoya *et al.* (2021) [57] studied the photocatalytic degradation of 9 $mg{\cdot}mL^{-1}$ polystyrene nanoparticles (PS-NPs) with the immobilized 1.3 cm^2 cop-

per oxide semiconductors Cu_2O/CuO at 30˚C ± 3˚C. The photocatalytic reactor was batch reactor equipped with a 50 W LED lamp with irradiation range 400 - 800 nm. The reactor was placed 15 cm from the lamp with a light intensity of 5.3 $mW \cdot cm^{-2}$. The photocatalysts were prepared by anodizing process rom two growth media (NH_4F and NaOH) with different morphologies and a bandgap between 1.6 and 2 eV. They reveal that immobilized Cu_2O/CuO were able to reduce 6-time higher concentration of PS-NPs (23%) with the 15% of mineralization, than by photolysis.

3.3.2. Future Perspectives

Photocatalytic degradation of polymeric materials implies the creation of oxidative species that stimulate the decomposition of organic components in the presence of water, oxygen and photons with sufficient energy. A large number of researches were carried out in the aqueous phase, with successful photocatalytic conversion of polymeric materials into products with added value, and recently more and more research has been oriented towards the solid phase in order to increase efficiency. Although there are still challenges to be overcome, solid-state photocatalysis (the integration of photosensitive materials into plastic materials) can improve mechanical, physical, and chemical properties and offers many advantages for plastic waste disposal. Furthermore, film thickness and particle size can prevent agglomeration. However, future research should be directed more toward examining the toxicity of semiconductors as well as value-added products.

4. Conclusion

This paper describes the division of plastic materials according to their size, and the listed plastic materials that are used in the world and that represent a great challenge when it comes to their disposal, recycling and treatment. A special challenge relates to plastic additives that are very harmful to humans and the environment. According to the data provided in the relevant databases, the trend of increasing plastic production in the last four years (2018-2021) is clearly visible. The methods of separation and degradation of micro- and nanoplastics that are used are presented. Special emphasis is placed on photocatalytic degradation with the use of metal oxide semiconductors based on zinc oxide and titanium dioxide. The degradation mechanism of polymer materials, but also the photocatalytic mechanism with the use of semiconductors, is presented. Hydroxyl radicals (·OH) and oxyanion radicals ($\cdot O_2^-$) are very responsible for the photocatalytic decomposition of plastic compounds. Various physical-chemical methods for the determination of the intermediate products produced in the process of photo-degradation enable the monitoring of polymer weight loss, changes in the morphological appearance, chemical composition and structure of micro- and nanoplastic waste.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Sophie, R.W., Pacome, G.K.K., Aminata, G., Kelety, C., Barthélemy, T., Vinciale, A.A.W., *et al.* (2024) Impact of Plastic Waste on the Human Health in Low-Income Countries: A Systematic Review. *Journal of Environmental Protection*, **15**, 572-595. https://doi.org/10.4236/jep.2024.155033

[2] Lamb, J.B., Willis, B.L., Fiorenza, E.A., Couch, C.S., Howard, R., Rader, D.N., *et al.* (2018) Plastic Waste Associated with Disease on Coral Reefs. *Science*, **359**, 460-462. https://doi.org/10.1126/science.aar3320

[3] Isobe, A., Azuma, T., Cordova, M.R., Cózar, A., Galgani, F., Hagita, R., *et al.* (2021) A Multilevel Dataset of Microplastic Abundance in the World's Upper Ocean and the Laurentian Great Lakes. *Microplastics and Nanoplastics*, **1**, Article No. 16. https://doi.org/10.1186/s43591-021-00013-z

[4] Murakami, T. and Tsuru, W. (2023) Research on Capture Performance of an Induction Type Microplastics Recovery Device. *Open Journal of Fluid Dynamics*, **13**, 81-91. https://doi.org/10.4236/ojfd.2023.132006

[5] Koelmans, A.A., Besseling, E. and Shim, W.J. (2015) Nanoplastics in the Aquatic Environment. Critical Review. In: Bergmann, M., Gutow, L. and Klages, M., Eds., *Marine Anthropogenic Litter*, Springer International Publishing, 325-340. https://doi.org/10.1007/978-3-319-16510-3_12

[6] Nguyen, B., Claveau-Mallet, D., Hernandez, L.M., Xu, E.G., Farner, J.M. and Tufenkji, N. (2019) Separation and Analysis of Microplastics and Nanoplastics in Complex Environmental Samples. *Accounts of Chemical Research*, **52**, 858-866. https://doi.org/10.1021/acs.accounts.8b00602

[7] Cooper, I. (2007) Plastics and Chemical Migration into Food. In: Barnes, K.A., Sinclair, C.R. and Watson, D.H., Eds., *Chemical Migration and Food Contact Materials*, Elsevier, 228-250. https://doi.org/10.1533/9781845692094.3.228

[8] (2023) BPF. https://www.bpf.co.uk/plastipedia/polymers/PVC.aspx

[9] Garcia, D.S., de Paula Amantes, B. and Tavares, M.I.B. (2023) Employment of Waste from the Textile Industry for the Production of Nanocomposites Aiming at the Generation of Thermal Shrinkable Films and the Non-Formation of Microplastics. *Materials Sciences and Applications*, **14**, 426-438. https://doi.org/10.4236/msa.2023.148028

[10] Statista (2023) Market Value of Plastics Worldwide in 2023, with a Forecast for 2033. Statista Research Market, Jan 28, 2024. https://www.statista.com/statistics/1060583/global-market-value-of-plastic/

[11] Wu, J., Lai, M., Zhang, Y., Li, J., Zhou, H., Jiang, R., *et al.* (2020) Microplastics in the Digestive Tracts of Commercial Fish from the Marine Ranching in East China Sea, China. *Case Studies in Chemical and Environmental Engineering*, **2**, Article ID: 100066. https://doi.org/10.1016/j.cscee.2020.100066

[12] Statista (2023) Annual Production of Plastics Worldwide from 1950 to 2022. Statista Research Department, Jan 25, 2023. https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/

[13] Plastics Europe (2022) Plastics—The Facts 2022. https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/

[14] Bratovcic A (2019) Degradation of Micro- and Nano-Plastics by Photocatalytic Methods. *Journal of Nanoscience and Nanotechnology Applications*, **3**, Article 304

[15] Kumar, V., Singh, E., Singh, S., Pandey, A. and Bhargava, P.C. (2023) Micro- and Nano-Plastics (MNPs) as Emerging Pollutant in Ground Water: Environmental

Impact, Potential Risks, Limitations and Way Forward towards Sustainable Management. *Chemical Engineering Journal*, **459**, Article ID: 141568. https://doi.org/10.1016/j.cej.2023.141568

[16] Hanif, M.A., Ibrahim, N., Dahalan, F.A., Md Ali, U.F., Hasan, M. and Jalil, A.A. (2022) Microplastics and Nanoplastics: Recent Literature Studies and Patents on Their Removal from Aqueous Environment. *Science of the Total Environment*, **810**, Article ID: 152115. https://doi.org/10.1016/j.scitotenv.2021.152115

[17] Patrício Silva, A.L. (2021) New Frontiers in Remediation of (Micro) Plastics. *Current Opinion in Green and Sustainable Chemistry*, **28**, Article ID: 100443. https://doi.org/10.1016/j.cogsc.2020.100443

[18] Nithin, A., Sundaramanickam, A., Bratovcic, A., Surya, P. and Sathish, M. (2022) Microplastics Occurrence in Different Regions around the World. In: Sillanpää, M., Khadir, A. and Muthu, S.S., Eds., *Microplastics Pollution in Aquatic Media*, Springer, 1-20. https://doi.org/10.1007/978-981-16-8440-1_1

[19] Bratovcic, A., Nithin, A. and Sundaramanickam, A. (2022) Microplastics Pollution in Rivers. In: Sillanpää, M., Khadir, A. and Muthu, S.S., Eds., *Microplastics Pollution in Aquatic Media*, Springer, 21-40. https://doi.org/10.1007/978-981-16-8440-1_2

[20] Hermabessiere, L., Dehaut, A., Paul-Pont, I., Lacroix, C., Jezequel, R., Soudant, P., *et al.* (2017) Occurrence and Effects of Plastic Additives on Marine Environments and Organisms: A Review. *Chemosphere*, **182**, 781-793. https://doi.org/10.1016/j.chemosphere.2017.05.096

[21] Zimmermann, L., Dierkes, G., Ternes, T.A., Völker, C. and Wagner, M. (2019) Benchmarking the *in Vitro* Toxicity and Chemical Composition of Plastic Consumer Products. *Environmental Science & Technology*, **53**, 11467-11477. https://doi.org/10.1021/acs.est.9b02293

[22] Nabi, I., Bacha, A., Ahmad, F. and Zhang, L. (2021) Application of Titanium Dioxide for the Photocatalytic Degradation of Macro- and Micro-Plastics: A Review. *Journal of Environmental Chemical Engineering*, **9**, Article ID: 105964. https://doi.org/10.1016/j.jece.2021.105964

[23] Zhang, F., Zhao, Y., Wang, D., Yan, M., Zhang, J., Zhang, P., *et al.* (2021) Current Technologies for Plastic Waste Treatment: A Review. *Journal of Cleaner Production*, **282**, Article ID: 124523. https://doi.org/10.1016/j.jclepro.2020.124523

[24] Jing, Y., Wang, Y., Furukawa, S., Xia, J., Sun, C., Hülsey, M.J., *et al.* (2021) Towards the Circular Economy: Converting Aromatic Plastic Waste Back to Arenes over a Ru/nb_2o_5 Catalyst. *Angewandte Chemie International Edition*, **60**, 5527-5535. https://doi.org/10.1002/anie.202011063

[25] Su, K., Liu, H., Zhang, C. and Wang, F. (2022) Photocatalytic Conversion of Waste Plastics to Low Carbon Number Organic Products. *Chinese Journal of Catalysis*, **43**, 589-594. https://doi.org/10.1016/s1872-2067(21)63885-8

[26] Chen, Z., Liu, X., Wei, W., Chen, H. and Ni, B. (2022) Removal of Microplastics and Nanoplastics from Urban Waters: Separation and Degradation. *Water Research*, **221**, Article ID: 118820. https://doi.org/10.1016/j.watres.2022.118820

[27] Shi, X., Zhang, X., Gao, W., Zhang, Y. and He, D. (2022) Removal of Microplastics from Water by Magnetic Nano-Fe_3O_4. *Science of the Total Environment*, **802**, Article ID: 149838. https://doi.org/10.1016/j.scitotenv.2021.149838

[28] Nikiema, J. and Asiedu, Z. (2022) A Review of the Cost and Effectiveness of Solutions to Address Plastic Pollution. *Environmental Science and Pollution Research*, **29**, 24547-24573. https://doi.org/10.1007/s11356-021-18038-5

[29] Lee, Q.Y. and Li, H. (2021) Photocatalytic Degradation of Plastic Waste: A Mini Review. *Micromachines*, **12**, Article 907. https://doi.org/10.3390/mi12080907

[30] Tian, L., Chen, Q., Jiang, W., Wang, L., Xie, H., Kalogerakis, N., *et al.* (2019) A Carbon-14 Radiotracer-Based Study on the Phototransformation of Polystyrene Nanoplastics in Water *versus* in Air. *Environmental Science*: *Nano*, **6**, 2907-2917. https://doi.org/10.1039/c9en00662a

[31] Zhao, X.u., Li, Z., Chen, Y., Shi, L. and Zhu, Y. (2007) Solid-Phase Photocatalytic Degradation of Polyethylene Plastic under UV and Solar Light Irradiation. *Journal of Molecular Catalysis A*: *Chemical*, **268**, 101-106. https://doi.org/10.1016/j.molcata.2006.12.012

[32] Yousif, E. and Haddad, R. (2013) Photodegradation and Photostabilization of Polymers, Especially Polystyrene: Review. *SpringerPlus*, **2**, Article No. 398. https://doi.org/10.1186/2193-1801-2-398

[33] Zhang, K., Hamidian, A.H., Tubić, A., Zhang, Y., Fang, J.K.H., Wu, C., *et al.* (2021) Understanding Plastic Degradation and Microplastic Formation in the Environment: A Review. *Environmental Pollution*, **274**, Article ID: 116554. https://doi.org/10.1016/j.envpol.2021.116554

[34] Singh, B. and Sharma, N. (2008) Mechanistic Implications of Plastic Degradation. *Polymer Degradation and Stability*, **93**, 561-584. https://doi.org/10.1016/j.polymdegradstab.2007.11.008

[35] Ali, S.S., Elsamahy, T., Koutra, E., Kornaros, M., El-Sheekh, M., Abdelkarim, E.A., *et al.* (2021) Degradation of Conventional Plastic Wastes in the Environment: A Review on Current Status of Knowledge and Future Perspectives of Disposal. *Science of the Total Environment*, **771**, Article ID: 144719. https://doi.org/10.1016/j.scitotenv.2020.144719

[36] Zhang, Q., Dandeneau, C.S., Zhou, X. and Cao, G. (2009) ZnO Nanostructures for Dye-Sensitized Solar Cells. *Advanced Materials*, **21**, 4087-4108. https://doi.org/10.1002/adma.200803827

[37] Noman, M.T., Amor, N., Petru, M., Mahmood, A. and Kejzlar, P. (2021) Photocatalytic Behaviour of Zinc Oxide Nanostructures on Surface Activation of Polymeric Fibres. *Polymers*, **13**, Article 1227. https://doi.org/10.3390/polym13081227

[38] ul Haq, A., Saeed, M., Gul Khan, S. and Ibrahim, M. (2022) Photocatalytic Applications of Titanium Dioxide (TiO_2). In: Ali, H.M., Ed., *Titanium Dioxide—Advances and Applications*, IntechOpen. https://doi.org/10.5772/intechopen.99598

[39] Bratovčić, A. (2023) Recent Achievements in Photocatalytic Degradation of Organic Water Contaminants. *Kemija u industriji*, **72**, 573-583. https://doi.org/10.15255/kui.2022.058

[40] Bratovcic, A. (2019) Photocatalytic Degradation of Organic Compounds in Wastewaters. *Technologica Acta*, **11**, 17-23. https://doi.org/10.5281/zenodo.2563022

[41] Ge, J., Zhang, Z., Ouyang, Z., Shang, M., Liu, P., Li, H., *et al.* (2022) Photocatalytic Degradation of (Micro) Plastics Using TiO_2-Based and Other Catalysts: Properties, Influencing Factor, and Mechanism. *Environmental Research*, **209**, Article ID: 112729. https://doi.org/10.1016/j.envres.2022.112729

[42] Nabi, I., Bacha, A., Li, K., Cheng, H., Wang, T., Liu, Y., *et al.* (2020) Complete Photocatalytic Mineralization of Microplastic on TiO_2 Nanoparticle Film. *iScience*, **23**, Article ID: 101326. https://doi.org/10.1016/j.isci.2020.101326

[43] Yuwendi, Y., Ibadurrohman, M., Setiadi, S. and Slamet, S. (2022) Photocatalytic Degradation of Polyethylene Microplastics and Disinfection of *E. coli* in Water over

Fe- and Ag-Modified TiO_2 Nanotubes. *Bulletin of Chemical Reaction Engineering & Catalysis*, **17**, 263-277. https://doi.org/10.9767/bcrec.17.2.13400.263-277

[44] Amato, P., Muscetta, M., Venezia, V., Cocca, M., Gentile, G., Castaldo, R., *et al.* (2023) Eco-sustainable Design of Humic Acids-Doped ZnO Nanoparticles for UVA/Light Photocatalytic Degradation of LLDPE and PLA Plastics. *Journal of Environmental Chemical Engineering*, **11**, Article ID: 109003. https://doi.org/10.1016/j.jece.2022.109003

[45] Razali, N., Wan Abdullah, W.R. and Mohd Zikir, N. (2020) Effect of Thermo-Photocatalytic Process Using Zinc Oxide on Degradation of Macro/Micro-Plastic in Aqueous Environment. *Journal of Sustainability Science and Management*, **15**, 1-14. https://doi.org/10.46754/jssm.2020.08.001

[46] Uheida, A., Mejía, H.G., Abdel-Rehim, M., Hamd, W. and Dutta, J. (2021) Visible Light Photocatalytic Degradation of Polypropylene Microplastics in a Continuous Water Flow System. *Journal of Hazardous Materials*, **406**, Article ID: 124299. https://doi.org/10.1016/j.jhazmat.2020.124299

[47] Lam, S., Chew, K., Sin, J., Zeng, H., Lin, H., Li, H., *et al.* (2022) Ameliorated Photodegradation Performance of Polyethylene and Polystyrene Films Incorporated with ZnO-PVP Catalyst. *Journal of Environmental Chemical Engineering*, **10**, Article ID: 107594. https://doi.org/10.1016/j.jece.2022.107594

[48] Díez, A.M., Pazos, M., Sanromán, M.Á., Naranjo, H.V., Mayer, J. and Kolen'ko, Y.V. (2023) Photocatalytic Solid-Phase Degradation of Polyethylene with Fluoride-Doped Titania under Low Consumption Ultraviolet Radiation. *Journal of Environmental Management*, **329**, Article ID: 117044. https://doi.org/10.1016/j.jenvman.2022.117044

[49] Raj, H., Bhatt, S., Laddha, S. and Rana, S. (2023) Ultrasonication-Aided Photocatalytic Degradation of Polyethylene. *Materials Today: Proceedings*, **72**, 500-506. https://doi.org/10.1016/j.matpr.2022.10.104

[50] Li, S., Xu, S., He, L., Xu, F., Wang, Y. and Zhang, L. (2010) Photocatalytic Degradation of Polyethylene Plastic with Polypyrrole/TiO_2 Nanocomposite as Photocatalyst. *Polymer-Plastics Technology and Engineering*, **49**, 400-406. https://doi.org/10.1080/03602550903532166

[51] Zhao, X.U., Li, Z., Chen, Y., Shi, L. and Zhu, Y. (2007) Solid-Phase Photocatalytic Degradation of Polyethylene Plastic under UV and Solar Light Irradiation. *Journal of Molecular Catalysis A*: *Chemical*, **268**, 101-106. https://doi.org/10.1016/j.molcata.2006.12.012

[52] Zhao, X., Li, Z., Chen, Y., Shi, L. and Zhu, Y. (2008) Enhancement of Photocatalytic Degradation of Polyethylene Plastic with CuPc Modified TiO_2 Photocatalyst under Solar Light Irradiation. *Applied Surface Science*, **254**, 1825-1829. https://doi.org/10.1016/j.apsusc.2007.07.154

[53] Wang, D., Zhang, P., Yan, M., Jin, L., Du, X., Zhang, F., *et al.* (2022) Degradation Mechanism and Properties of Debris of Photocatalytically Degradable Plastics LDPE-TiO_2 Vary with Environments. *Polymer Degradation and Stability*, **195**, Article ID: 109806. https://doi.org/10.1016/j.polymdegradstab.2021.109806

[54] Kaewkam, P., Kanchanapaetnukul, A., Khamyan, J., Phadmanee, N., Lin, K.A., Kobwittaya, K., *et al.* (2022) UV-Assisted TiO_2 Photocatalytic Degradation of Virgin LDPE Films: Effect of UV-A, UV-C, and TiO_2. *Journal of Environmental Chemical Engineering*, **10**, Article ID: 108131. https://doi.org/10.1016/j.jece.2022.108131

[55] Olajire, A.A. and Mohammed, A.A. (2021) Bio-Directed Synthesis of Gold Nanoparticles Using *Ananas comosus* Aqueous Leaf Extract and Their Photocatalytic Ac-

tivity for LDPE Degradation. *Advanced Powder Technology*, **32**, 600-610. https://doi.org/10.1016/j.apt.2021.01.009

[56] Ariza-Tarazona, M.C., Villarreal-Chiu, J.F., Hernández-López, J.M., Rivera De la Rosa, J., Barbieri, V., Siligardi, C., *et al.* (2020) Microplastic Pollution Reduction by a Carbon and Nitrogen-Doped TiO_2: Effect of pH and Temperature in the Photocatalytic Degradation Process. *Journal of Hazardous Materials*, **395**, Article ID: 122632. https://doi.org/10.1016/j.jhazmat.2020.122632

[57] Acuña-Bedoya, J.D., Luévano-Hipólito, E., Cedillo-González, E.I., Domínguez-Jaimes, L.P., Hurtado, A.M. and Hernández-López, J.M. (2021) Boosting Visible-Light Photocatalytic Degradation of Polystyrene Nanoplastics with Immobilized Cu_xO Obtained by Anodization. *Journal of Environmental Chemical Engineering*, **9**, Article ID: 106208. https://doi.org/10.1016/j.jece.2021.106208