

Biodegradable Polymer-Supported Titanium Dioxide Photocatalysts

Subjects: Environmental Sciences

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During the past two decades, immobilization of titanium dioxide (TiO₂), a well-known photocatalyst, on several polymeric substrates has extensively gained ground since it limits the need of post-treatment separation stages. Taking into account the numerous substrates tested for supporting TiO₂ photocatalysts, the use of biodegradable polymer seems a hopeful option owing to its considerable merits, including the flexible nature, low price, chemical inertness, mechanical stability and wide feasibility.

Keywords: biodegradable polymers ; titanium dioxide ; immobilization ; photocatalysis ; wastewater remediation

1. Introduction

Water contamination by organic compounds and metals has been outlined as one of the major global problems nowadays. In fact, due to their non-biodegradable nature, these harmful compounds remain for long time periods after their discharge into the environment, thus being characterized as persistent contaminants. Several techniques have been explored to remove these pollutants from water, including adsorption and photocatalysis, which comprise attractive and eco-friendly approaches. The nano-sized titanium dioxide (TiO₂) is a famous photocatalyst among the metal oxides, due to its excellent efficiency, low price, physicochemical stability, extensive disposal, safety, and non-corrosive behavior. It has three crystal forms, anatase, rutile and brookite, while the first presents the most effective photocatalytic performance. Nevertheless, due to the challenges that arise from the very small particle size and the unfeasible reusability of the particles, including the post separation and recovery of the photocatalytic particles after water or wastewater treatment, the need of TiO₂ immobilization is crucial ^[1] (Figure 1).

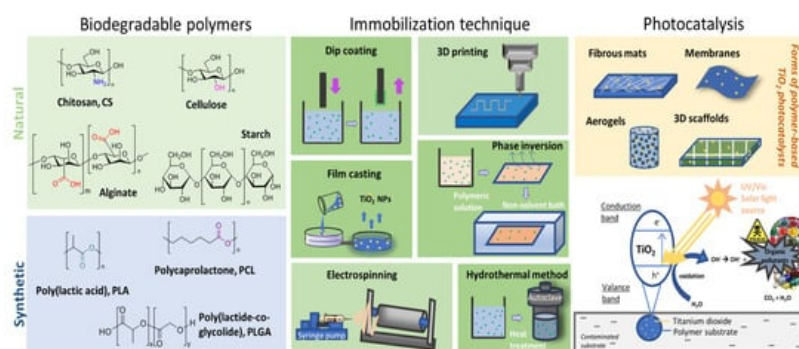


Figure 1. A brief illustration of the main synthetic routes fabricated for the immobilization of TiO₂ nanoparticles onto biodegradable polymeric substrates for the photocatalytic degradation of organic pollutants.

2. Biodegradable Polymers Combined with TiO₂ for Enhanced Photocatalytic Activity

2.1. Natural Biodegradable Polymers

2.1.1. Chitosan (CS)

Synthetic and Characterization Routes

A biodegradable polymer that has been widely explored in green pathways for waste remediation and photocatalytic activities is chitosan (CS). It is a linear polysaccharide and one of the most abundant biopolymers in the nature, with biodegradable, biocompatible and non-toxic character, derived from the deacetylation process of chitin, found in the exoskeletons of crustaceans and arthropods. Enzymes, such as chitosanase or lysozymes, are known to degrade

chitosan. Its low-cost and the several versatile properties that chitosan possesses, render this polymer as an ideal candidate for environmental remediation purposes. Since CS is a great supporting material for the dispersion of TiO₂ nanoparticles, CS/TiO₂ is one of the most investigated composite photocatalysts, while their synergistic effects between them have also been studied. The immobilization of TiO₂ in CS films has been widely investigated since it can be easily obtained owing to the miscibility between CS and hydrophilic TiO₂. Chitosan contains in its structure amino and hydroxyl functional groups which act as coordination sites to form complexes with metals and several compounds, boosting by this means the effective removal of pollutants with special selectivity. However, the immobilization attempts require strong affinity between the TiO₂ and the substrate, and thus, cross-linking processes with the aid of several alkaline agents (e.g., NaOH) are often selected [2]. A brief description of the studies reported herein for CS-supported photocatalysts is presented in **Table 1**.

Table 1. Summary of the chitosan-supported TiO₂ photocatalysts enclosed in the presented literature.

Biodegradable Polymeric Matrix						Photocatalysis Parameters.		Degradation Efficiency (Time Required)	Ref.
No.	Polymer Substrate	TiO ₂ Precursor	Dopant	Immobilization Technique	Morphology of the Photocatalyst	Type of (Target) Pollutant	Light Source		
1	CS	TiO ₂ nanopowders (Aeroxide; 80% anatase)	MT	CS-MT film casting & dip-coating in TiO ₂ formulation	Bilayer photocatalyst	Methyl orange dye	45 W fluorescent lamp	98.7%	[2]
2	CS-grafted poly(vinyl imidazole)	Titanium isopropoxide	CDs	In situ deposition of TiO ₂ NPs and CDs onto the polymeric surface under microwave irradiation	Nanocomposite hydrogel	2,4-dichlorophenol Reactive Blue 4 Reactive Red 15	Sunlight exposure for 30 min	95% (180 min) 95.8% (30 min) 98.2% (30 min)	[4]
3	CS	TiO ₂ (P25)	-	Immobilization of TiO ₂ in CS film by cross-linking process	Film	Tetracycline hydrochloride	UV lamp 30 W and $\lambda = 360$ nm	87% (240 min)	[2]
4	CS	Aeroxide P25-TiO ₂	-	3D printing	3D printed scaffolds	Amoxicillin	UV irradiation (125 W), $\lambda = 300-800$ nm	90–60% (180 min)	[5]

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- In other cases, the inclusion of organic supports, carbon nanofillers, such as carbon dots (CDs) [4], graphene oxide (GO) [7], carbon nanotubes [10] and other metal oxides [8], into the polymer matrix has been also explored, providing photocatalytic materials with excellent architecture and dispersion of the nanofillers. Carbonaceous and inorganic materials not only perform as supporting materials for the new composites but also act as co-catalysts for the intensification of the photocatalytic efficiency of TiO₂ [12].
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- Figure 2.** (a) Schematic illustration of electrospinning system, (b) nanofibers generation by single needle electrospinning, (c) demonstration of large-scale nanofibers mat and (d) scheme modeling the preparation of algae decorated TiO₂/Ag hybrid nanofiber membrane. Reprinted with permission from [9].

2. Photocatalytic Performance of Biodegradable Polymer Matrix

- Structural, optical and photocatalytic behaviors. *J. Sol-Gel Sci. Technol.* 2016, 80, 793–801.
- Chitosan based composites achieved a wide range of degradation efficiency reaching 90% in most of the cases, while UV radiation was most frequently employed for the degradation of pollutants. Different structures of chitosan-based materials and structural characteristics of starch/polyvinyl alcohol/nano-titania photocatalytic antimicrobial composite films. *Lwt* were used in photocatalytic experiments, such as films, bilayers, 3D printed scaffolds and fibers. Another important factor

is the USA 704-712. Chitosan based catalysts were applied for 3–6 cycles in

the majority of studies with sufficient results. However, a decrease in the photocatalytic activity was recorded after the second cycle in most of studies. Nevertheless, Babudín et al. investigated the photodegradation of methyl orange (MO), nanoparticles and their photocatalytic activities. *J. S. Adv.* 2017, 7, 48083–48094

in which the reusability of TiO₂/CS-Mt composite was tested for 10 cycles. According to this study, two chitosan bilayers were manufactured with or without the addition of Mt. The insertion of Mt showed a favorable effect in charge separation of pure anatase carbon doped titanium dioxide: A. efficient visible light active photocatalyst Low temperature synthesis of TiO₂. Thus, these bilayers performed a higher photocatalytic performance in degradation of MO dye. pure anatase carbon doped titanium dioxide: An efficient visible light active photocatalyst. Mater. Sci. Semicond.

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Figure 3: Schematic image for the mechanism of photoinduced charge carrier transfers in TiO₂-Au cellulose membranes under solar irradiation. Reprinted with permission of Reference [44].

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studied under UV and visible light irradiation, while their degradation efficiency ranged between 70% and 90% [46], [45]. Kreetachat, T.; Kruenate, J.; Suwannahong, K. Preparation of TiO₂/Bio-composite film by sol-gel method in VOCs after 180–360 min of treatment. Moreover, other toxic pollutants were examined such as stearic acid, Cr(VI), and photocatalytic degradation process. Appl. Mech. Mater. 2013, 390, 552–556.

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2.1.3. Alginate (Alg)

Synthetic and Characterization Routes

Retrieved from <https://engr.cdnlib.com/entry/history/show/30735>.
Alginate is a natural and anionic polysaccharide, mainly derived from the cell walls of algae. In recent years, the low price and abundance in nature, have rendered the alginate as a polymer of much attention. Due to the presence of hydroxyl and carboxyl groups on its molecule, alginate has been as well explored for the effective removal of metal ions.

Gelation techniques are commonly chosen for the preparation of alginate-based photocatalysts. Within an innovative effort, Dalponte et al. [21] reported on the synthesis of a buoyant alginate photocatalyst with immobilized TiO₂ nanoparticles for accomplishing both superior photocatalytic behavior and more feasible separation after treatment

processes. The ionotropic gelation technique was employed, with CaCO₃ or NaHCO₃ gas-forming agents added firstly to a TiO₂ dispersion with the addition of a sodium alginate solution (**Figure 4**).



Figure 4. (a) Scheme from ionotropic gelation and CO₂ generation from both gas forming agents (CaCO₃ and NaHCO₃), (b) bubbles held within the gel beads with CaCO₃ in its formulation, and (c) floating TiO₂/CaAlg beads with 1:1 ratio of NaHCO₃/alginate and 1:1 ratio of CaCO₃/alginate [24].

Photocatalytic Performance

Getting an insight into bibliography of alginate-based materials with combination of TiO₂ nanoparticles, it is observed that they were used for various applications, such as the photo-degradation of common dyes (MO, basic blue 41, tartrazine, RhB), removal of pharmaceuticals (ibuprofen, and sulfamethoxazole), and other organic compounds (2-naphthol). Moreover, alginate-TiO₂ nanocomposites were used in different morphologies including fibers, membranes, hydrogel spheres, and papers. The irradiation was carried out under two main sources, UV light or sunlight for a time range between 45–340 min. Photocatalytic materials based on alginate showed a high recyclability with a range of 3–7 cycles [22][24][23][24][25][26][27].

2.1.4. Starch

Synthetic and Characterization Routes

Starch is a renewable material with biocompatible and biodegradable nature, low cost and high abundance, and due to this positive profile, it has been widely explored in food, textile, packaging as well as pharmaceutical industries. It mainly consists of amylose and amylopectin, while one of the most challenging chapters concerning its use is its dissolution since the strong inter- and intra-molecular hydrogen bonds and its semicrystalline nature with double helices, require strong polar systems. Biodegradation of starch can mainly proceed via hydrolysis at the acetal bonds by enzymes.

Photocatalytic Performance

Regarding the literature of starch-based TiO₂ materials for the removal of different pollutants from wastewater through photocatalytic process, it was noticed that researchers mainly focused on MB and rhodamine B (RhB) dyes removal, widely used in textile industry. In most studies UV light and/or sunlight radiation was employed for the degradation of different initial concentration of dyes, ranging from 4 to 50 ppm [28][29][30][31][32]. The removal of contaminants ranged within 94–100% in most of the cases, and treated solutions were exposed to irradiation for 90 to 360 min.

2.2. Synthetic Polymers with Biodegradable Nature

2.2.1. Poly(Lactic Acid) (PLA)

Synthetic and Characterization Routes

PLA is one of the most dynamic and promising biodegradable synthetic polymers derived from renewable resources, such as corns, sugar beets, wheat and other starch-based products. It can be synthesized mainly by the polycondensation of lactic acid or by ring opening polymerization of lactide with the aid of a catalyst. PLA is totally degraded under compost conditions. Except its wide use in pharmaceutical technology, the fabrication of PLA for the synthesis of TiO₂-immobilized photocatalytic materials has limited literature, which is presented below, in brief. The synthetic pathways for these photocatalysts include mainly casting, electrospinning and spin-coating methods.

Photocatalytic Performance

In the field of bio-based polymers, PLA has also been used for the fabrication of TiO₂ composite materials with photocatalytic activity. Three interesting studies used the synthesized composites for the degradation of pharmaceuticals (mainly antibiotics) [33][34][35], while another group of studies examined the degradation of common dyes such as MB and methylene orange [36][37][38]. The polymeric materials, acting as supports for the photocatalysts, were mainly manufactured in two morphologies: films and nanofibers. The degradation efficiency of pollutants ranged within different levels. The degradation of pharmaceuticals was near to 90% in most of cases, while the photocatalytic degradation of the azo dyes

varied mostly between 70% and 90%. The photocatalytic experiments were carried out under UV and sunlight irradiation, while an adsorption step was priorly applied. A wide range of irradiation times was applied starting from 2 to 10 h.

2.2.2. Polycaprolactone (PCL)

Synthetic and Characterization Routes

PCL (polycaprolactone) is a semi-crystalline aliphatic polyester produced by a ring-opening polymerization of ϵ -caprolactone, mainly in the presence of tin octanoate as catalyst. It is soluble in many organic solvents, while it possesses a semi-rigid nature in room temperature conditions. Enzymes and fungi simply degrade PCL, while for the enhancement of its biodegradation several copolymers with lactide or glycolide are proposed. Due to its low melting point, advanced rheological and viscoelastic characteristics, PCL has been extensively explored in the manufacture of electrospun porous fibers. Only recently PCL was reported as a template to prepare PCL/TiO₂ fibrous mats as dynamic candidates for efficient photocatalysts and thus further exploration in this field should be investigated.

Photocatalytic Performance

According to the available bibliography, PCL-TiO₂ composites were applied for the degradation of organic dyes including MB, RhB, and Reactive Black 5 or even for disinfection from bacteria often found in wastewater effluent, such as *E. Coli*, *C. albicans*, and *Staphylococcus aureus*. The PCL composites were manufactured in different structures for photocatalytic purposes, including nanofibers and membranes. Most experiments were carried out under UV light radiation with treatment time ranging from 80–300 min according to the targeted pollutants and the photocatalytic material used. Moreover, the reusability of materials was monitored up to three cycles exhibiting satisfactory results [39][40][41][42][43][44].

2.2.3. Other Synthetic Polymers

There are also few biodegradable polymers which have been explored to prepare photocatalysts for TiO₂ immobilization, but the relative reports are limited (Table 2).

Table 2. Summary of other synthetic polymer-supported TiO₂ photocatalysts enclosed in the presented literature.

Biodegradable Polymeric Matrix						Photocatalysis Parameters			Ref.
No.	Polymer Substrate	TiO2 Precursor	Dopant	Immobilization technique	Morphology of the Photocatalyst	Type of (Target) Pollutant	Light Source	Degradation Efficiency (Time Required)	
1	PLA + PBAT + PBS	Titanium isopropoxide (97 wt%)	-	- Sol-gel method for theTiO2 nanoparticles - blown film technique	Composite films	Toluene	Photocatalytic oxidation reactor with UV-C lamp 6 W and λ = 254 nm	52% (270 min)	[45]
2	PLGA	TiO2 nanopowder	-	Air-liquid foaming technique	Porous 3D-PCL scaffolds	Methylene blue E. Coli	UV lamp light with wavelength 365 nm	90% (180 min) ~99% (24 h)	[46]
3	PHB & CS oligomers	Titanium (IV) oxide (nano-TiO2) (99.7% anatase nanopowder)	-	Electrospinning/Electrospraying & Impregnation techniques	Hybrid fibrous materials	Methylene Blue Escherichia Coli	UV light (UVASPOT 400/T, Dr. Honle AG; UV lamp UV 400 F/2; 400 W)	>92% (180 min) 100% (30–60 min)	[47]

Abbreviations: CS, chitosan; PBAT, polybutylene adipate-co-terephthalate; PBS, poly(butylene succinate); PLA, poly(lactic acid); PLGA, poly(lactide-co-glycolide); PHB, poly(3-hydroxybutyrate).

One of them is poly(lactide-co-glycolide) (PLGA), which is a copolymer of poly(lactic acid) (PLA) and poly(glycolic acid) (PGA). It is a biodegradable and biocompatible polyester with tunable mechanical properties; merits that led Pelaseyed et al. [46] to utilize it for the fabrication of 3D porous PLGA/TiO₂ nanocomposite scaffolds. Air-liquid foaming technique was employed to manufacture the very porous nanocomposite scaffolds with the PLGA/10 wt% TiO₂ being the optimal product, whereas a high photocatalytic efficiency against methylene blue dye was also confirmed, amongst the other beneficial properties of the final composite scaffolds.

Poly(3-hydroxybutyrate) (PHB) is another interesting biodegradable polymer which is easily degraded by numerous microorganisms (bacteria, fungi, algae) under several conditions. With an innovative concept, PHB combined with CS oligomers were utilized for the fabrication of fibrous photocatalysts with TiO₂ nanoparticles incorporated. Researchers used a grouping of electrospinning, electrospraying and impregnation methods, which potentially ensure the desired architecture of the fibrous scaffolds [47].

3. Conclusions

TiO₂-induced photocatalysis considerably remains as the most efficient and feasible option for the photo-degradation of persistent organic pollutants, including mainly pharmaceuticals, azo dyes, toxic metals and pathogenic microorganisms present in water and wastewater. Constant efforts are performing to modify the TiO₂ photocatalyst and provide materials highly effective in visible light in accordance with their ease post-treatment recovery. Several research articles have been published in which biodegradable polymers were facilitated to manufacture eco-friendly and sufficient photocatalytic materials against several target pollutants, especially from wastewater. Several methods were applied like sol-gel, film casting, electrospinning, spin coating and 3D printing, transfusing photocatalytic efficiency, mechanical strength and reusability to the fabricated composites. Fibers, membranes and aerogels fabricated from biodegradable polymers, presented different advantages in their overall performance. In fact, the pollutants' removal can be fulfilled by the synergistic effects of the biodegradable polymer-based adsorption and the redox reactions induced by the photo-generated charge carriers, created on the surface of TiO₂.

Future studies should be focusing on new methodologies and combined techniques for the application of biodegradable polymers, as to prepare chemical and thermal resistant polymer-supported/TiO₂ composite materials, with advanced architecture and superior reusability, recyclability and photocatalytic performance. Moreover, the facilitation of green practices for the preparation of the photocatalysts should also be taken into consideration. More research and work are still needed for the categorization of the appropriate manufacturing and TiO₂ anchoring techniques for each biodegradable polymer, since each of them possesses a special character with specific chemical and physical properties.

Despite the fact that exceptional studies are found in the literature including the preparation and photocatalytic activity of several polymer-based/TiO₂ materials for remediation of wastewater, these works are performed in the laboratory environment and not at large scale. Biodegradable polymer-supported TiO₂ materials should be further researched and advanced, exceptionally in the visible light region. Thus, a lot of effort should also be extended for the commercialization of the prepared photocatalysts, under real conditions.