

Review

# Catalytic Composite Systems Based on N-Doped TiO<sub>2</sub>/Polymeric Materials for Visible-Light-Driven Pollutant Degradation: A Mini Review

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**Abstract:** This mini review summarizes the preparation and testing of polymeric composites with a N-doped TiO<sub>2</sub> photocatalyst to effectively design a photocatalytic system for water pollutant degradation under visible light. In detail, the various N-doped TiO<sub>2</sub>/polymer composites reported in the literature are briefly discussed along with some examples dealing with the use of N-doped TiO<sub>2</sub> particles, both supported on the external surface of polymers and dispersed within the structure of visible-light-transparent polymeric aerogels. Finally, the scope for future works and challenges for the commercialization of such materials are highlighted.

**Keywords:** N-doped TiO<sub>2</sub>; polymeric supports; photocatalysis; visible light; water and wastewater



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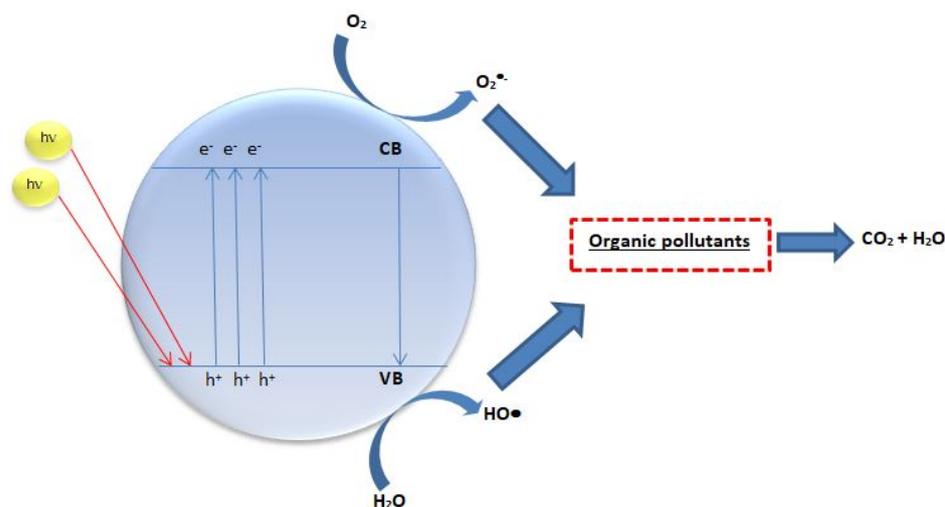
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## 1. Introduction

In recent years, one of the most important issues of researchers and society has been health and environmental protection via the sustainable use of natural resources, such as water. Indeed, the progressive decrease in clean water sources is due to increasing overpopulation and serious water pollution due to human activities. Currently, approximately 1.1 billion people worldwide lack access to fresh water, and 2.7 billion people have scarce water for at least one month of the year, based on data collected by the World Wide Fund for Nature (WWF) [1]. One possible solution to such problems is to develop effective treatment methods for removing pollutants at such a level that water can be reused. Unfortunately, conventional pollution remediation methods show limited performance [2]. For this reason, the interest of the scientific community has been focused on alternative methods, such as “advanced oxidation processes (AOPs)”. Among the AOPs, heterogeneous photocatalysis has been the focus of considerable attention in recent years due to the relative ease of the process [3].

Photocatalysis is commonly defined as a phenomenon leading to the alteration of the rate of a chemical reaction by light or other electromagnetic radiation. Photocatalysts are typically semiconductors due to their ability to absorb suitable radiation, promoting the chemical transformation of selected substrates [4,5]. The most commonly used photocatalysts are metal oxides, which do not have available energy levels in the valence band. Instead, the energy levels of the empty conduction band are available. The energy that separates the valence and conduction bands is called the band gap ( $E_g$ ). Activation of a photocatalyst is achieved through the absorption of a photon with high band gap energy, which results in the promotion of an electron from the valence band into the conduction band and in the simultaneous generation of a hole in the valence band [6].

The charge carriers can migrate to the semiconductor surface and be transferred to adsorbed molecules, thereby initiating reduction or oxidation processes (Figure 1).



**Figure 1.** General semiconductor photocatalysis mechanism.

Heterogeneous photocatalysis represents one of the main challenges in the field of treatment and decontamination of water, air and antimicrobial materials, with applications in healthcare environments [7], because it is able to work at ambient temperatures and atmospheric pressures. Moreover, this method does not transfer the pollutant from one phase to another, as in the case of certain conventional treatment techniques (such as adsorption), but rather eliminates the target compound [8,9]. Usually, semiconductors including TiO<sub>2</sub>, WO<sub>3</sub>, ZnO, CdS and ZnS are selected as photocatalysts due to their electronic structure involving narrow band gaps [10–18]. Among the different semiconductors, TiO<sub>2</sub> is almost the only material suitable for industrial use at present and also probably in the future. This is because TiO<sub>2</sub> has the most efficient photoactivity, the highest stability and the lowest cost [19].

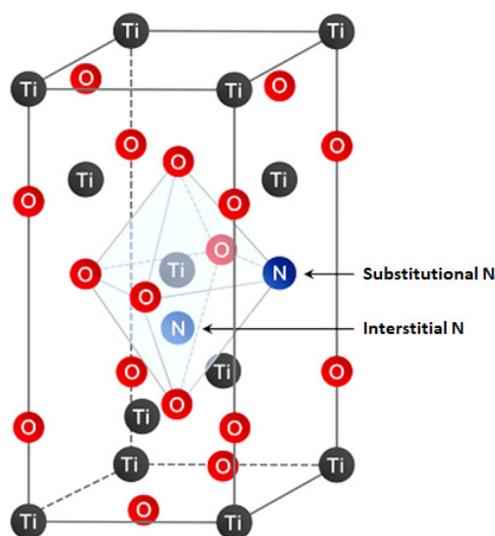
However, the major factors limiting both photocatalytic efficiency and activity of TiO<sub>2</sub> are listed below:

- the  $E_g$  of anatase TiO<sub>2</sub> is 3.2 eV, i.e., it absorbs light in the UV region, so that only a small portion (5%) of sunlight can be used for a photocatalytic process. This is a great limitation in its use as a photocatalyst for the conversion of solar energy into chemical energy [20];
- As in all photocatalysts, photogenerated electron–hole pairs undergo fast recombination in competition with charge transfer to chemical species adsorbed on the catalyst surface [21], which, however, can be solved thanks to the formulation of heterojunctions between two semiconductors [22];
- In the case of water and wastewater treatment, the use of slurry reactors limits the industrial applications of photocatalysis, since the necessary separation of catalyst powders after liquid-phase reactions is troublesome and expensive [23,24].

## 2. Why N-Doped TiO<sub>2</sub> for Heterogeneous Photocatalysis?

Since one of the main drawbacks of heterogeneous photocatalysis is the scarce photoactivity of TiO<sub>2</sub> under visible light, which limits its use for practical applications, many efforts have been made to narrow the band gap of TiO<sub>2</sub> and to shift its optical response to the visible-light region. Considerable interest has been focused on TiO<sub>2</sub> doping with non-metal ions, especially with nitrogen. Many papers addressing the effect of the doping of TiO<sub>2</sub> with nitrogen on the catalytic activity of a large variety of chemical reactions performed under visible-light irradiation are reported in the literature [7,25–31]. The presence of nitrogen in the TiO<sub>2</sub> lattice induces significant photoactivity under visible light, but the exact mechanism for this enhancement is still elusive [7]. It is well-known that the incorporation of nitrogen into the TiO<sub>2</sub> framework occurs in two ways: substitutional and interstitial. In a more detailed sense, substitutional doping implies the replacement of

oxygen with nitrogen element [32], whereas interstitial doping is based on the addition of a nitrogen element into the  $\text{TiO}_2$  lattice [31], as reported in Figure 2.



**Figure 2.** Model structure of the nitrogen atom in the anatase  $\text{TiO}_2$  lattice.

Irie et al. [33] argued that oxygen sites substituted by a nitrogen atom induce the generation of new electron-occupied energy levels above the valence band (VB) of  $\text{TiO}_2$ . As a consequence, the irradiation with UV light excites electrons of both the VB and the new energy levels, whereas the electrons in the energy levels generated by the doping with nitrogen can be excited by visible light alone [34]. The modification mechanism of anatase doped with non-metal elements was also analysed in detail by Zhao et al. [35]. They concluded that  $\text{TiO}_2$  doped with substitutional nitrogen generates electron acceptor states above the VB. In contrast,  $\text{TiO}_2$  doped with interstitial nitrogen promotes the formation of isolated impurity states in the middle of  $\text{TiO}_2$  Eg. However, it is not possible to exclude the simultaneous occurring of both substitution and interstitial doping depending on the preparation procedure adopted for the synthesis of N-doped  $\text{TiO}_2$ .

Finally, in addition to the visible light response induced by doping, it was also shown that the introduction of nitrogen into the  $\text{TiO}_2$  lattice may also suppress the recombination phenomena of the photogenerated electron–hole pairs [36,37].

### 3. Immobilization of N-Doped $\text{TiO}_2$ on Polymeric Supports

Despite the growing interest of researchers in the development of active visible-light semiconductors, photocatalysis has not yet found widespread use in practice. For example, the photocatalytic treatment of water using  $\text{TiO}_2$ -based nanoparticles involves aqueous suspensions that require an additional process [9]. To solve this issue, attempts are made to immobilize semiconductor nanoparticles in various matrices, including polymer supports.

The first study that reports the use a polymeric support for photocatalysts was performed by Tennakone et al. in 1995 [38]. The authors supported undoped  $\text{TiO}_2$  on polyethylene (PE) films by adopting a simple, thermal treatment method.

Since then, many polymeric substrates have been studied for immobilizing  $\text{TiO}_2$  photocatalysts. The main reason for the immobilization was to find suitable macroscopic supports for overcoming the post-treatment recovery of powder photocatalysts in order to develop large-scale photocatalytic systems to be used for water and wastewater systems.

Many polymers with different features, such as a hydrophobic nature [39], low-cost [40], chemical inertness, mechanical strength, low-density and durability, were tested for the immobilization of undoped  $\text{TiO}_2$  [41]. Table 1 summarizes various types of polymers with their physical–chemical properties. However, it must be considered that such systems can be activated only by UV light. Recent studies have been focused on the supporting

provided to N-doped TiO<sub>2</sub> by various polymeric substrates, such as polyvinylidene fluoride (PVDF) [42], polypropylene (PP) [43], polytetrafluoroethylene (PTFE) [44], polyaniline (PANI) [45] and polystyrene (PS) [46–50]. Many authors reported that the coupling of semiconductors with polymers improves the photoactivity of N-doped TiO<sub>2</sub> for the degradation of water pollutants as well as for the inactivation of bacteria under visible-light irradiation (Table 2).

**Table 1.** Various types of polymers used as support.

Polymers	Physical–Chemical Properties	Ref.
PTFE	Hydrophobic, narrow pore size, better porosity and excellent mechanical strength	[51]
PANI	Environmentally stable, nontoxic and low-cost	[52]
PVDF	Electroactive polymer	[42]
PET	Good mechanical and thermal durability, inherently non-absorptive to water, resilient to wrinkling as well as shrinking and resistant to most chemicals	[53]
PP	Good mechanical and physical properties, lightweight and high melting point, among others	[54]
PS	Cheap, inert, non-toxic and low-density thermoplastic	[46]

**Table 2.** List of recently reported immobilized N-doped TiO<sub>2</sub> photocatalyst on polymers.

Polymers	Method of Synthesis	Pollutant	Light Sources	Ref.
PTFE	Solvothermal	Methylene blue	Halogen lamp, 300 W	[44]
PANI	PPMSG method	Acid Red 73	Halogen lamp, 300 W	[45]
PVDF	Magnetron sputtering	RED 41	Xenon lamp, 150 W	[42]
PET	Hydrothermal process	Methylene blue	Xenon lamp, 300 W	[53]
PP	Dip-coating process	<i>E. coli</i> , <i>S. aureus</i> and MRSA	-	[43]
PP	Low-temperature hydrothermal method	Methyl orange	Xenon lamp, 150 W	[41]
PS	Solvent-casting method	Methylene blue, <i>E.coli</i>	-	[46]
PS	Solvent-casting method	Carbamazepine, diclofenac and trimethoprim	Solar light	[47]
PS	Solvent-casting method	Methylene blue	White LEDs	[48]
PS	Solvent-casting method	<i>E.coli</i>	Solar light	[49]
PS	Solvent-casting method	Urea	White LEDs	[50]
sPS	Gelation of a catalyst in a polymeric substrate and subsequent extraction with supercritical CO <sub>2</sub>	Methylene blue, phenol	White LEDs, 5 W	[55,56]

#### 4. General Overview on Methods for the Immobilization of N-Doped TiO<sub>2</sub> on Polymeric Supports

As reported in the literature, polymeric materials are relatively easy to be used as an effective substrate for the immobilization of a photocatalyst [57]. The methods for fixing N-doped TiO<sub>2</sub> particles on the chosen polymeric substrate can be developed starting from those studied for the immobilization of undoped TiO<sub>2</sub>. They may vary from simple, such as

the solvent-casting method [46–50] or sol–gel techniques [58], to more complex, specialized and expensive methods, such as magnetron sputtering [59] and gelation of a catalyst in a polymeric substrate and subsequent extraction with supercritical CO<sub>2</sub> [55,56,60]. It is worth noting that the method for immobilizing N-doped TiO<sub>2</sub> on a polymeric support influences the photocatalytic activity, which also depends on the type of substrate and pollutant to be degraded. For instance, it is not possible to use thermal treatments characterized by an incredibly high temperature to modify or degrade the polymer's chemical structure. Indeed, the conventional methods usually employed for the coating process on inorganic supports require heating at temperatures higher than 300 °C to obtain a crystallinity degree of an immobilized photocatalyst able to induce a significant photoactivity towards the pollutant degradation [57].

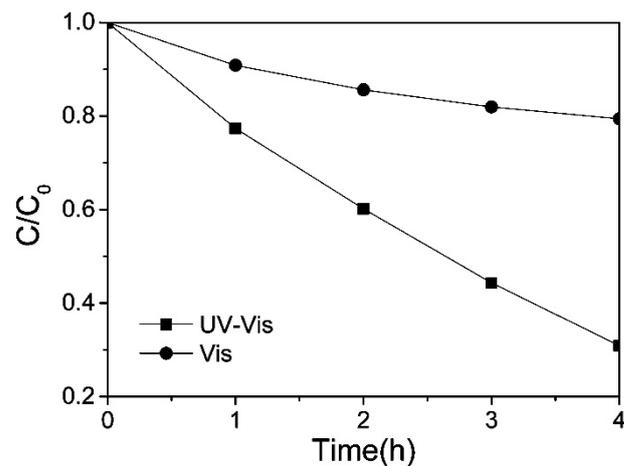
Until today, sol–gel and sputtering methods are the most studied and applied low-temperature deposition techniques for anchoring nanoparticles on various polymeric substrates [57]. However, even if the sol–gel method is easy to use, the photocatalytic activity of such obtained systems is generally very low, if compared to other preparation methods [41]. It is argued that the negative results can be attributed to the amorphous crystal phase obtained for N-doped TiO<sub>2</sub> particles, due to the limitation of the calcination temperature for the post-deposition thermal treatment. This limits the application of sol–gel methods to supporting N-doped TiO<sub>2</sub> only on polymeric substrates with high thermal stability [58]. Otherwise, it is suggested to prepare crystalline N-doped TiO<sub>2</sub> films on polymeric supports through coating procedures starting from suitable dispersion made by a N-doped TiO<sub>2</sub> powder mixed with an appropriate organic binder [61]. Indeed, the absence of appropriate binding sites, commonly due to low surface energy of polymers, implies a low adhesion of N-doped TiO<sub>2</sub> and consequently offers difficulty in surface coating [62]. In fact, it is significantly difficult to achieve a well-adhered, crack-free coating, since the polymeric substrates are generally relatively hydrophobic [61]. In this sense, surface pre-treatment could improve the adhesion of N-doped TiO<sub>2</sub> on the polymeric substrate. To this aim, different methods, such as surface etching [63] or deposition of an intermediate layer [64], have been recently proposed.

## 5. Applications of N-Doped TiO<sub>2</sub> on Polymeric Supports as Visible-Light-Active Photocatalytic Systems

Some examples of photocatalytic systems realized by modifying polymeric materials with N-doped TiO<sub>2</sub> are described below.

### 5.1. N-Doped TiO<sub>2</sub>/PP (Polypropylene)

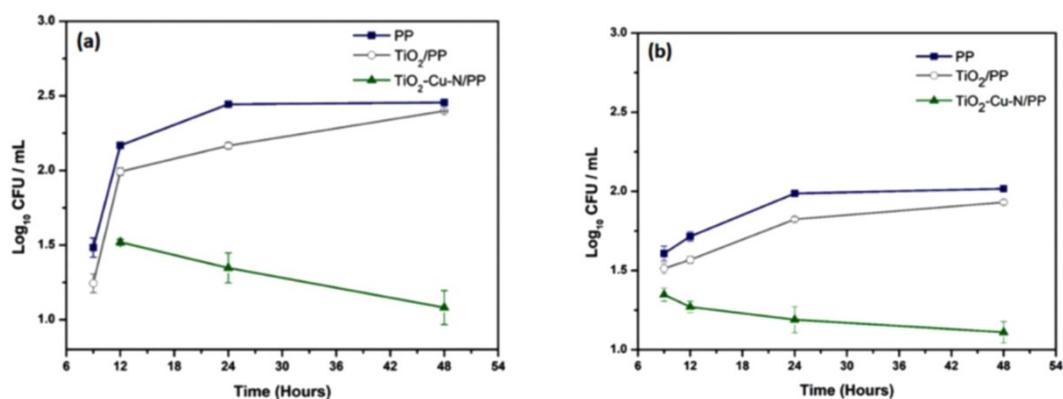
Polypropylene (PP) is a thermoplastic material which is characterized by good mechanical and physical properties in addition to being lightweight. It is used in a variety of applications, such as packaging for consumer products, plastic parts for various industries including the automotive industry, medical supplies such as catheters and syringes in addition to textiles, such as films and non-woven fibers [65]. Han et al. [41] prepared a N-doped TiO<sub>2</sub> photocatalyst supported on PP in a granular form using a low-temperature hydrothermal method. N-doped TiO<sub>2</sub> was first prepared by the sol–gel method using triethylamine (TEA) as nitrogen dopant source. The prepared photocatalysts was then immobilized on a PP substrate (NdT/PP composite) in a hydrothermal reactor (T= 150 °C) via a simple one-step process. The photocatalytic activity of the NdT/PP composite was finally evaluated, analyzing the methyl orange (MO) decolorization under both UV and visible irradiation (Figure 3).



**Figure 3.** Decolorization of the MO dye by N-doped TiO<sub>2</sub> on PP granules under UV and visible-light (Vis) irradiation. Reprinted with permission from [41]. Copyright 2009, American Chemical Society.

The results showed lower photo-oxidation activity of the NdT/PP composite for the MO dye compared to the photocatalyst in powder form due to the relatively lower content of N-doped TiO<sub>2</sub> on PP granules and the smaller surface area of the NdT/PP composite as compared to the NdT powder particles. The obtained data suggest the preparation method is obviously not suitable for obtaining an efficient catalytic system.

C. Betancur-Henao et al. prepared TiO<sub>2</sub> co-doped with copper and nitrogen (TiO<sub>2</sub>-Cu-N) through the wet impregnation method, using urea as a nitrogen precursor and copper nitrate as a copper precursor. The obtained TiO<sub>2</sub>-Cu-N particles were ground in a mortar and mixed with distilled water and acetyl acetone. The obtained suspension was further diluted with distilled water and the catalyst was then immobilized on PP in the form of discs (diameter: 14 mm, height: 4 mm) through the dip-coating technique [43]. The dip-coating was performed by controlling the immersion velocity. The obtained discs were dried in an oven at 80 °C for 30 min. The photocatalytic results under visible-light irradiation demonstrated the antibacterial activity of TiO<sub>2</sub>-Cu-N/PP against Gram-negative and Gram-positive bacteria as well as their potential use in biomedical applications (Figure 4) [43].



**Figure 4.** Viable cell counts (Log CFU ml<sup>-1</sup>) of the bacterial strains (a) *S. aureus* and (b) *E. coli* over time on coated and uncoated PP discs [43].

### 5.2. N-Doped TiO<sub>2</sub>/PS (Polystyrene)

Polystyrene (PS) is a thermoplastic polymer largely used in food service and the retail industry [46]. Some papers report the immobilization of undoped TiO<sub>2</sub> on polystyrene for the removal of different water pollutants under UV light [66,67] and under solar light [68]. However, also in the case of PS as a support, still scarce is the literature concerning the use of this polymer as a support for N-doped TiO<sub>2</sub>, despite, in recent years, this topic having

started to be considered by some research groups. Indeed, the solvent-casting method was applied to support N-doped TiO<sub>2</sub> particles on the surface of PS discs [46]. Specifically, a N-doped TiO<sub>2</sub> suspension in acetone was dropped on the PS support followed by drying at room temperature. Chemical–physical characterization results and visible-light-driven methylene blue degradation tests evidenced that the best performances are achieved when an optimal N-doped TiO<sub>2</sub> amount is dispersed in acetone to obtain a suspension that is dropped on the PS surface [46]. Starting from these preliminary results, N-doped TiO<sub>2</sub> was also immobilized on the surface of PS spheres and PS pellets in cylindrical shape by using the same preparation method [48–50]. The photocatalytic activity under visible light of such systems was evaluated in the methylene blue and urea degradation as well as in the inactivation of *E. coli* in real municipal wastewater, evidencing the stability of the obtained systems after several reuse cycles [48–50]. However, a photocatalytic activity lower than that observed for the powder forms of photocatalyst is generally observed [31]. Moreover, when N-doped TiO<sub>2</sub> is used in powder form in slurry reactors, the photocatalytic activity is negatively influenced because of the strong tendency of photocatalyst particles to form a large aggregate size in an aqueous solution [69].

#### 5.2.1. N-Doped TiO<sub>2</sub>/Syndiotactic Polystyrene (s-PS) Monolithic Aerogels

It is worthwhile to note that, even if it is possible to arrange suitable preparation methods for the effective immobilization of N-doped TiO<sub>2</sub> particles on the external surface of polymeric supports, there are some features that can inhibit their use in large-scale photocatalytic systems for water and wastewater treatment. For example, when N-doped TiO<sub>2</sub> is immobilized in granular form or as a thin film on a polymeric surface, the absorption of the light by the support itself may occur and the accessibility of the catalytic surface to the photons can be worsened, inducing photocatalytic activity significantly lower than that observed when N-doped TiO<sub>2</sub> is used in powder form [70,71].

As an alternative, crystalline powders of N-doped TiO<sub>2</sub> can be immobilized and dispersed within the structure of visible-light-transparent polymeric aerogels, starting from a gel obtained from a dispersion of photocatalyst particles in an organic solvent for the polymer and followed by extraction in supercritical CO<sub>2</sub> [55,56,60].

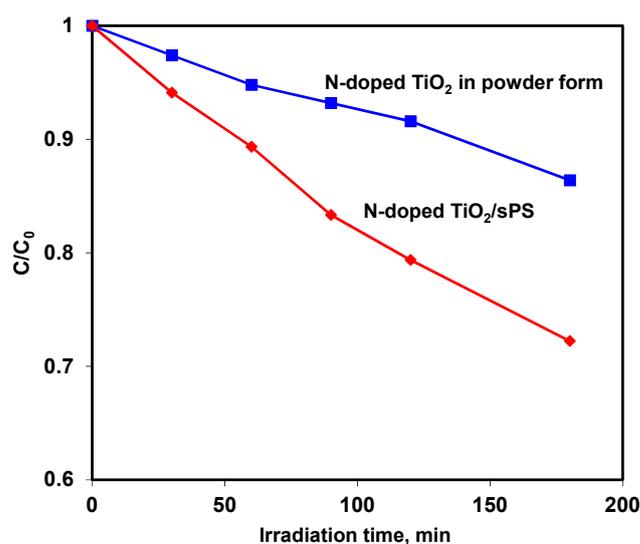
Therefore, starting from the interesting results observed for carbon-gel-modified TiO<sub>2</sub> [72], polymeric aerogels have attracted tremendous attention in recent years due to their very high specific surface area and recoverability after the treatment step as a consequence of their macroscopic size [73].

In particular, syndiotactic polystyrene (s-PS) monolithic aerogels are especially appealing since they offer many benefits over typical polymeric supports, such as a high surface area and high transparency to visible light.

Therefore, the use of s-PS aerogels allows the preservation of the photocatalytic properties of N-doped TiO<sub>2</sub> in powder form, minimizing the aggregation phenomena between photocatalyst particles that typically occur in slurry photocatalytic reactors, as pointed out above. Moreover, the N-doped TiO<sub>2</sub>/s-PS monolithic structure can also avoid the expensive and time-consuming separation processes, necessary for powder photocatalysts separation, allowing a scale-up of a photocatalytic system activated by visible light to be realized [60].

In addition, it is very important to underline that the hydrophobic nature of s-PS aerogels also protects the photocatalyst from inhibition mechanisms, such as surface blockage, photocorrosion and dissolution in an aqueous medium. Moreover, the s-PS aerogel matrix is selectively penetrable only by non-polar molecules, giving the composite a selectivity in the removal of pollutants that the N-doped TiO<sub>2</sub> catalyst alone does not possess [74].

All the previous features were confirmed by recent papers in the literature. In particular, N-doped TiO<sub>2</sub> dispersed in syndiotactic polystyrene (s-PS) monolithic aerogels showed photocatalytic degradation efficiency higher than N-doped TiO<sub>2</sub> powders towards the degradation of both the methylene blue dye (Figure 5) and phenol [55,56].



**Figure 5.** Comparison of photocatalytic activity of N-doped TiO<sub>2</sub>/sPS with respect to N-doped TiO<sub>2</sub> powdered catalyst in the removal of methylene blue [55].

This result was attributed to an efficient dispersion of N-doped TiO<sub>2</sub> in the composite aerogels, avoiding the aggregation phenomena between photocatalyst particles.

### 5.3. N-Doped TiO<sub>2</sub>/PET (Polyethylene Terephthalate)

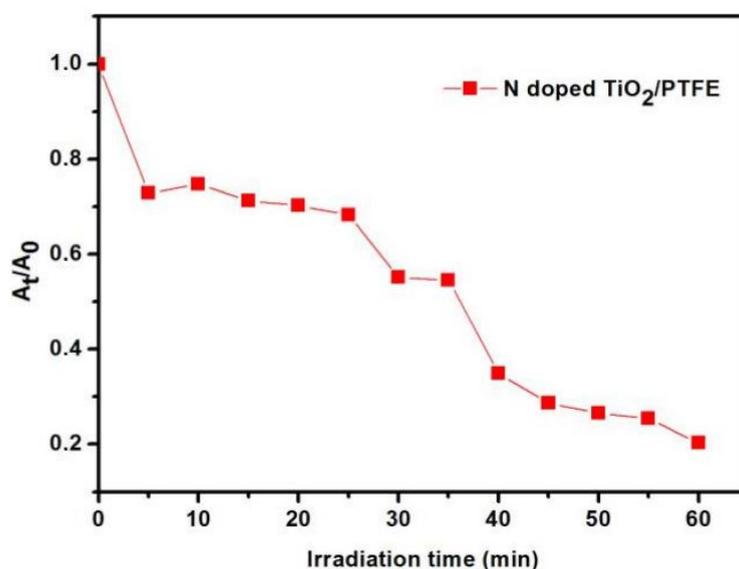
Polyethylene terephthalate (PET) is among those plastics which are an important part of our everyday life. It is an important commercial thermoplastic polymer, with applications ranging from packaging, fabrics and films to molded parts for automobiles, electronics and many more. The use of PET as a support material for photocatalysts may represent a matter of interest from both economic and environmental perspectives, since PET is a low-cost, recyclable material, has very good mechanical properties (e.g., flexibility) and is resistant to most chemicals, allowing the realization of different forms of photocatalytic reactors [75]. An example, the photocatalytic performance of PET bottles coated with undoped TiO<sub>2</sub> was studied by Hereida and Duffy et al. [76]. These bottles can be used for solar water disinfection, because TiO<sub>2</sub> combines the action of solar disinfection and an advanced oxidation process, improving the effectiveness of these technologies [76]. Unfortunately, relatively little research is found in the literature about N-doped TiO<sub>2</sub> photocatalyst coated on PET for photocatalytic applications.

Recently, PET filaments functionalized with N-doped TiO<sub>2</sub> nanoparticles were investigated by Zhang et al. The PET filaments were loaded with N-doped TiO<sub>2</sub> prepared by a hydrothermal process. In detail, 4 mmol of titanium sulfate (precursor of TiO<sub>2</sub>) was dissolved in 40 mL of deionized water at an ambient temperature. Then, 8 mmol of urea (nitrogen dopant source) was subsequently added into the precursor solution; finally, 0.8 g of PET filaments was dipped into the precursor solution at a liquid ratio of 1:50 for 10 min, and then transferred to a 50 mL PTFE-lined container. The photocatalytic activity of the N-doped TiO<sub>2</sub>/PET samples was analyzed in the degradation of methylene blue dye [53]. The results evidenced a remarkable photocatalytic activity in the presence of visible light.

### 5.4. N-Doped TiO<sub>2</sub>/PTFE (Polytetrafluoroethylene)

A fluorocarbon polymer, such as polytetrafluoroethylene (PTFE), was used in many fields because it has high flexibility and temperature stability and is corrosion-resistant. PTFE has the lowest material surface energy known, with an excellent resistance to chemical reagents. The surface of a PTFE plate has a static water contact angle of 108°, and a slide angle >90°, indicating water adhesion to the PTFE surface. F. N. Aini et al. [44] prepared a N-TiO<sub>2</sub>/PTFE composite by using a modified solvothermal method with urea as the nitrogen source.

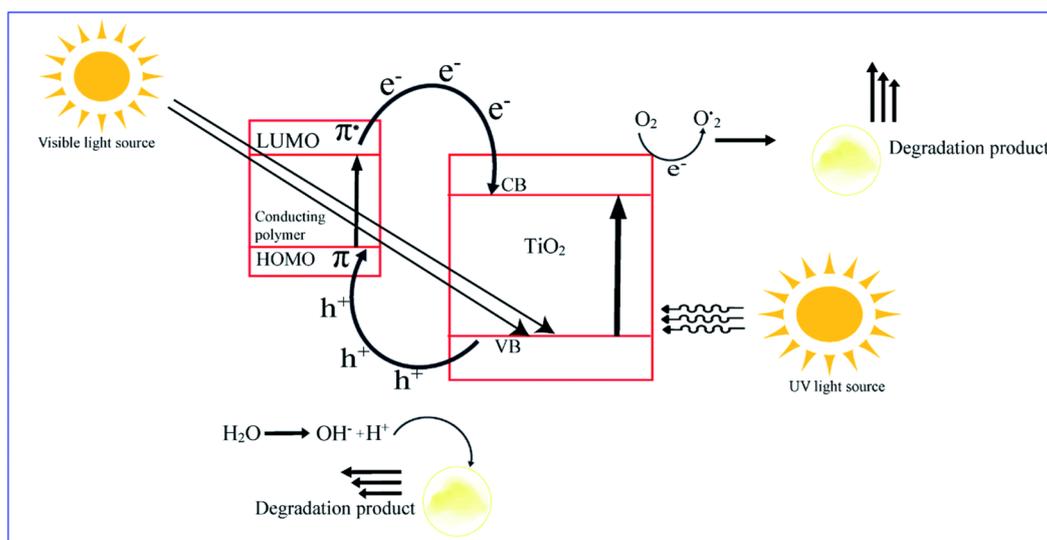
The performances of N-TiO<sub>2</sub>/PTFE were evaluated in the decolourization of organic dye (methylene blue) (Figure 6). The results showed that after 1 h of visible-light irradiation, almost 80% of methylene blue was removed. Moreover, the authors underlined that the addition of nitrogen into the TiO<sub>2</sub> lattice increases photocatalytic activity under visible light, whereas PTFE contributes to significant photoactivity thanks to its high contact angle.



**Figure 6.** Photodegradation kinetic of methylene blue under visible-light irradiation using N-doped TiO<sub>2</sub>/PTFE [44]. Content from [44] is used under the terms of the Creative Commons Attribution 3.0 license.

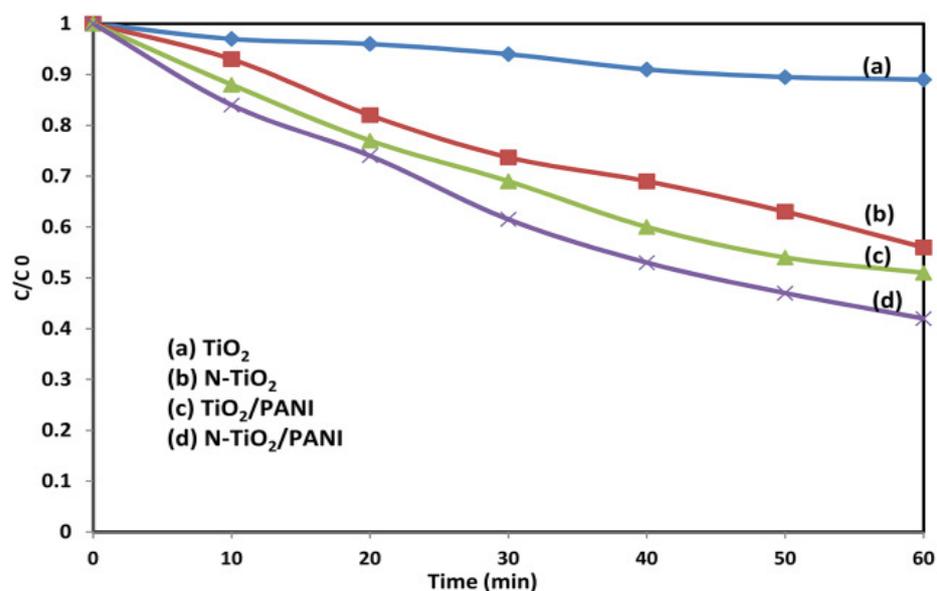
### 5.5. Conducting-Polymer-Based Photocatalysis

Recently, conducting polymers (CPs) as photosensitizers for semiconductor materials have been proven to immensely enhance photodegradation. In fact, nanocomposites of CPs, both with metals and metal oxides, showed excellent photocatalytic efficiency for removing organic contaminants, including dyes and PPCPs under both UV light and natural sunlight irradiation [77]. When CPs are exposed to light irradiation, a  $\pi$ - $\pi^*$  transition occurs [78]. This means that photogenerated electrons become excited to the  $\pi^*$  orbital of CPs, which have almost the same energy of the TiO<sub>2</sub> CB band. The photogenerated electron can easily migrate from CPs to TiO<sub>2</sub>. Consequently, the electrons can react with water and oxygen to produce  $\cdot$ OH and O<sub>2</sub><sup>-</sup>, which cause the oxidation of the contaminants. In the same way, h<sup>+</sup> migrates from the VB of TiO<sub>2</sub> to the high energy state of CPs. The photogenerated holes migrate to the surface of the photocatalyst, and oxidation of the contaminants occurs (Figure 7).



**Figure 7.** Photocatalytic mechanism in conducting polymer composites. Reproduced from [79] with permission from the Royal Society of Chemistry.

It is reported that, in general, the coupling of a semiconductor ( $\text{TiO}_2$ ) with a suitable conducting polymer such as polyaniline (PANI) [80] results in a synergistic effect that hinders the charge carrier recombination process and increases  $\text{TiO}_2$  activity under UV irradiation. To date, there are still few papers regarding the coupling of CPs with N-doped  $\text{TiO}_2$ . In particular, Mohammad Vaez et al. have prepared N- $\text{TiO}_2$ /PANI nanocomposites by the polymerization of aniline in acidic media using ammonium persulfate in the presence of nanocrystalline N-doped  $\text{TiO}_2$  particles for the degradation of the Acid Red 73 under visible-light irradiation [45]. The authors evidenced the enhancement of photocatalytic degradation of N- $\text{TiO}_2$ /PANI nanocomposites compared to N-doped  $\text{TiO}_2$  or PANI only (Figure 8). The authors attributed the results to the presence of nitrogen in the  $\text{TiO}_2$  framework that can create an electron-occupied intraband gap, which results in the charge transfer between the conduction band and the valence band of  $\text{TiO}_2$  under visible light [81].



**Figure 8.** Effect of  $\text{TiO}_2$ , N- $\text{TiO}_2$ ,  $\text{TiO}_2$ /PANI and N- $\text{TiO}_2$ /PANI on the degradation of Acid Red 73 under visible light (initial concentration of dye: 10 mg/L, pH 6.5, and concentration of  $\text{H}_2\text{O}_2$ : 0.55 mg/L) [45].

C. J. Tavares et al., in order to increase the photocatalytic efficiency of titania coatings, immobilized N-doped TiO<sub>2</sub> on polyvinylidene fluoride (PVDF) by unbalanced reactive magnetron sputtering. The photocatalytic activity was evaluated by the degradation of Red 41 dye. The authors underlined that the simultaneous presence of the N-doped photocatalyst and the PVDF leads to an increase in the photocatalytic activity [42]. In particular, the optimized sample leads to Red 41 degradation of almost 20% after 400 min of visible-light irradiation.

## 6. Concluding Remarks and Perspectives

Heterogeneous photocatalysis mediated by TiO<sub>2</sub>-based semiconductors is the most promising technical solution for the removal of organic contaminants present in water and wastewater. The two main drawbacks limiting the practical applications of the photocatalytic processes based on TiO<sub>2</sub> are the poor photoactivity under visible light of the non-doped TiO<sub>2</sub>-based semiconductors and their use in powder form, which makes recovery difficult. In recent years, many efforts have been made by researchers both to shift the optical response of TiO<sub>2</sub> from the UV region to that of visible light, and to immobilize photocatalysts on macroscopic supports with the aim of improving the efficiency and performance of this class of photocatalysts. As a result, immobilizing N-doped TiO<sub>2</sub> on the external surface of different polymer supports proved to be a very effective approach to obtain active visible-light photocatalysts, which perform the degradation of a wide variety of organic pollutants. Additionally, to support N-doped TiO<sub>2</sub> on suitable polymeric surfaces, new materials with peculiar properties, such as both being waterproof and self-cleaning under indoor- or solar-light irradiation, could be created. These materials may be suitable to realize personal protective equipment with self-sanitizing action. This approach is particularly intriguing in regard to the fight against the COVID-19 virus, being able to reduce the contagion risk. This technical solution may reduce the spread of human pathogens and help to prevent cases of acquired infection, which are the cause of much concern in healthcare environments.

Unfortunately, some drawbacks such as the hydrophobicity of the polymer supports, their low surface energy as well as the lack of surface anchoring points for the N-doped TiO<sub>2</sub> make this approach remain a challenge. Although methods of polymer surface pre-treatment, such as surface etching or intermediate layer deposition, are reported and discussed in the literature, more efficient solutions for surface pre-treatment should be figured out in order to improve the adhesion of N-doped TiO<sub>2</sub> on the polymer substrate. In this sense, a practical and effective approach (such as corona pre-treatment) could be to activate polymer surfaces by introducing suitable functional groups which allow the realization of stable, N-doped TiO<sub>2</sub> films.

As for photocatalytic water treatment, when N-doped TiO<sub>2</sub> is immobilized in granular form or as a thin film on a polymeric surface, the absorption of the light by the support itself may occur and, as a consequence, the accessibility of the catalytic surface to the photons can be worsened, inducing photocatalytic activity significantly lower than that observed when N-doped TiO<sub>2</sub> is used in powder form. To overcome these drawbacks, monolithic high-porosity polymeric aerogels as hosts for N-doped TiO<sub>2</sub> particles may be an interesting approach. Indeed, the available literature has shown that the use of aerogels can allow the preservation of the photocatalytic properties of N-doped TiO<sub>2</sub> in powder form. Although polymer aerogels functionalized with N-doped TiO<sub>2</sub> were successfully tested for the photocatalytic degradation of water pollutants under visible light, the preparation methods were only realized on a laboratory scale. Further studies should aim to develop low-cost and simple methods for their preparation on large scale. Additionally, future works should be addressed to testing these materials under direct sunlight with the aim to also find suitable kinetic laws that can be utilized in the design of large-scale solar photocatalytic reactors.

Very promising materials for photocatalysts in environmental applications are obtained by the incorporation of conducting polymers with N-doped TiO<sub>2</sub>. In fact, conducting

polymers can assure a synergistic effect with N-doped TiO<sub>2</sub> that hinders the charge carrier recombination process and increases the photoactivity under visible light. Although advances have been made to increase the photoresponse of such photocatalytic systems in the visible region of the spectrum, thorough studies on their light-responsive range and carrier separation capacity should still be conducted in order to optimize their properties. Finally, so far only a few conducting polymers, especially PANI, have been investigated for N-doped TiO<sub>2</sub>/conducting polymers as catalytic systems. It is desirable that future studies will also focus on other types of conductive polymers to design efficient materials as photocatalysts in environmental applications.

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