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Effects of Fe^{3+} and Ag^{+} ions on the photocatalytic degradation of sucrose in water

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Abstract

The photocatalytic oxidation of sucrose in the presence of dissolved Fe^{3+} and Ag^{+} ions in titanium dioxide suspensions under near-UV illumination has been investigated. The oxidation of sucrose to carbon dioxide was enhanced in the presence of these metal ions at low atom:atom percentage concentrations. An optimum metal ion loading was observed for both silver (2.0 atom%) and iron (1.0 atom%) ions. Beyond the optimum metal loading, the activity of silver-modified TiO_2 particles was lowered. In the case of iron-modified TiO_2, the activity of the catalyst (5.0 atom% Fe^{3+}) was lower than that of bare TiO_2. The role of metal ions in photocatalytic reactions is a function of the type of the metal and its concentration in the system. Different mechanisms are responsible for the effects of different metal ions added to titanium dioxide suspensions.

Keywords: Photocatalysis; Titania; Fe^{3+}; Ag^{+}; Wastewater treatment

1. Introduction

Toxic organic compounds and heavy metals found in industrial or domestic wastewater effluents must be removed or destroyed to an acceptable level, before discharge to receiving waters. Heterogeneous photocatalysis is a process, which has potential for the rapid, non-selective oxidation of a broad range of organic compounds [1]. Organic compounds are destroyed to carbon dioxide, water and simple mineral acids or inorganic ions [1].

Heterogeneous photocatalysis involves the use of a combination of oxygen, UV light and a photocatalyst such as titanium dioxide (TiO_2) to effect a chemical reaction. In order to improve the low quantum yields of photocatalytic processes, attempts have been made to enhance the performance of TiO_2 as a photocatalyst using noble metals. Modification of the photocatalyst surface with metal deposits has been reported to improve or retard catalyst activity [2–5]. It is therefore necessary to understand the influential role of metal deposits in photoreactions.

In this work, the photocatalytic oxidation of sucrose was studied in the presence of dissolved iron(III) ions and silver(I) ions in titanium dioxide suspensions. Sucrose was chosen as a model compound in this study since it is a simple compound with no hetero-atoms,

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such as S, Cl, P, that can interfere with the rate of photooxidation [6–8]. Attempts have been made here to understand the mechanism by which these metal ions in solution alter the activity of titanium dioxide.

2. Experimental

In all experiments, titanium dioxide was used as the photocatalyst (Degussa P25, 80% anatase, 20% rutile, 50 m^2/g, primary particle size ~25–30 nm, agglomerate size ~100 nm). Suspensions of the photocatalyst (0.2 wt.%, 30 ml), adjusted to pH 3.5, were circulated through a slurry type spiral photoreactor [9]. The light source employed was a 20 W blacklight blue fluorescent tube (300–400 nm emission range, maximum emission at ~350 nm). The mass of sucrose (in terms of carbon (C) atoms) degraded was 2000 μg (66.7 μg/ml). The degradation of sucrose was monitored by measuring the amount of carbon dioxide generated during the reaction. Carbon dioxide evolved was detected by an online conductivity meter [9]. The rate of change in conductivity was converted to the rate of carbon dioxide generation.

To prepare silver- and iron-modified photocatalysts, known amounts of either $Fe(NO_3)_3$ or $AgNO_3$ were added during the preparation of the TiO_2 suspensions. Atomic absorption spectroscopy (AAS) was used to determine the quantity of metal ions deposited on the surface of the photocatalyst. Transmission electron microscopy (TEM) was used to examine catalyst particles after surface modification. TEM examination yielded information such as the location and size of the metal deposits. X-ray diffraction (XRD) was used to identify the species formed on the surface of the modified catalyst.

3. Results and discussion

3.1. Mineralization of sucrose using iron-modified Degussa P25

The photooxidation of 2000 μg C sucrose was enhanced when Fe^{3+} ions were added to TiO_2 suspensions. The optimum metal ions concentration was 1.0 atom% (Fig. 1). The maximum sucrose photooxidation rate was 1.4 times greater (at the optimum conditions) than the maximum oxidation rate achieved in the absence of Fe^{3+} ions. Optimum Fe^{3+} loadings have been observed in other studies too [10–13].

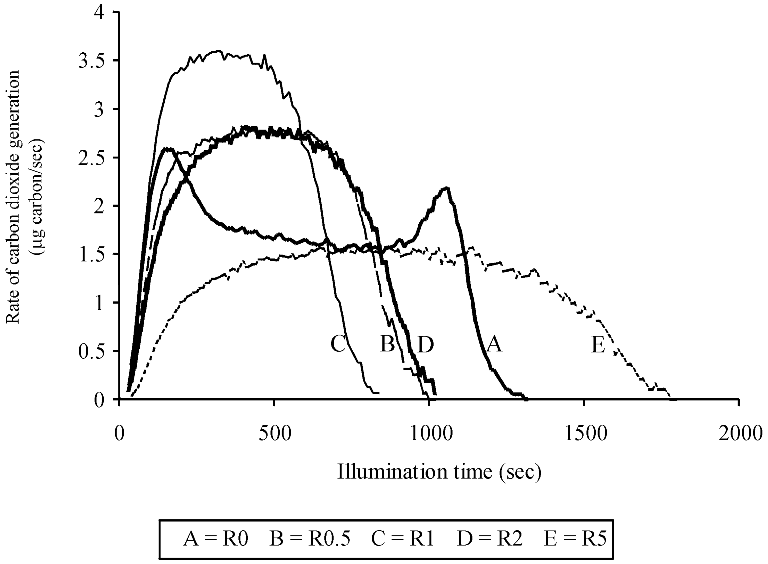


Fig. 1. Plot showing the effect of Fe^{3+} concentration on sucrose oxidation (atomic percent of Fe^{3+} with respect to Ti^{4+} (R) are 0.5, 1, 2, and 5, respectively).

The beneficial effect of Fe^{3+} ions is attributed to electron trapping at the semiconductor surface. The trapping of photoelectrons leaves photogenerated holes available for reaction with hydroxyl ions to form hydroxyl radicals:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \tag{1}$$

Decreased activity above the optimum metal ions concentration is possibly due to the oxidation of Fe^{2+} ions by hydroxyl radicals or holes

$$Fe^{2+} + h^{+} \rightarrow Fe^{3+} \tag{2}$$

The competition for holes by Fe^{2+} ions and OH^{-} ions means that less hydroxyl radicals are generated for the oxidation of organic molecules. This short-circuiting phenomenon has been previously suggested by several researchers [13,14]. The cyclic process between Fe^{2+} and Fe^{3+} ions may even proceed without the further generation of hydroxyl radicals. Thus excess Fe^{3+} ions in solution may have a negative effect on the photooxidation reaction.

During illumination of the suspension in the absence of sucrose, Fe^{3+} ions in solution were found to precipitate as iron hydroxide, $Fe(OH)_3$ at pH 3.5. The presence of iron hydroxides would have decreased the rate of photocatalytic oxidation by reflecting UV light as a result of increased solution opacity [1,11,15]. Excessive amounts of iron hydroxides may explain the detrimental effect of high iron(III) concentrations (5.0 atom%) in our system. After the oxidation of sucrose, a higher concentration of iron ions was measured in the suspension by AAS analysis. It is thought that sucrose molecules trap holes, leaving electrons available to reduce Fe^{3+} ions in $Fe(OH)_3$ to Fe^{2+} ions. Thus Fe^{2+} ions are released into solution.

At lower Fe^{3+} concentrations, smaller amounts of iron hydroxides were present. However, the photoreaction was still enhanced. The effect of light reflection due to the presence of $Fe(OH)_3$ at or less than the optimum Fe^{3+} loading may not be severe enough to retard the reaction, but it becomes a dominant factor at high iron concentrations.

An alternative route in which Fe^{3+} ions enhance the oxidation of organics is the photo-Fenton reaction [10–12,16]. Ferrous ions can be generated either via Eq. (3) with light of wavelength, $\lambda < 580\,\mathrm{nm}$:

$$Fe^{3+} + H_2O + h\nu \rightarrow OH^{\bullet} + Fe^{2+} + H^{+} \tag{3}$$

or via the trapping of electrons by ferric ions on the semiconductor surface. For the photo-Fenton reaction to proceed, the presence of hydrogen peroxide is required. Due to the difficulty in reducing oxygen to form H_2O_2 on illuminated TiO_2 particles [13], H_2O_2 may be generated via the following pathways in the presence of ferrous ions at low pH or under acidic conditions [16,17]:

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet -} \tag{4}$$

$$O_2^{\bullet -} + H^{+} + e^{-} \rightarrow HO_2^{\bullet} \tag{5}$$

$$HO_2^{\bullet} + Fe^{2+} + H^{+} \leftrightarrow H_2O_2 + Fe^{3+} \tag{6}$$

It has been suggested that ferric ions, produced according to Eq. (4), react with hydrogen peroxide generating hydroxyl radicals and ferrous ions. The consumption of Fe^{2+} and Fe^{3+} ions in this cycle continues as the suspension is irradiated [17]. So in irradiated aqueous TiO_2 suspensions in the presence of Fe^{3+} ions, two sources of hydroxyl radical generation are possible [10]. However, since the quantity of hydrogen peroxide formed via Eq. (6) is not clearly known, the mechanism of the photo-Fenton reaction in our system is less probable. It was also found that under similar conditions [10,11], the removal rate of organics in homogeneous systems was considerably lower than in TiO_2 photocatalytic systems. Hence the contribution of homogeneous reactions in enhancing the heterogeneous photooxidation of sucrose may not be significant.

3.2. Mineralization of sucrose using silver-modified Degussa P25

The influence of silver ions on the photodegradation of sucrose in aqueous TiO_2 suspensions at pH 3.5 was investigated. As shown in Fig. 2, the maximum sucrose oxidation rate was obtained in the presence of 2.0 atom% Ag^{+} ions (optimum metal ion loading). At this Ag^{+} concentration, the improvement in the maximum oxidation rate was almost double, when compared to the pure TiO_2 system.

Further increases in silver ion concentration gave no additional improvements in catalyst activity. Rather, catalyst activity decreased slightly. However, at all Ag^{+} loadings used in this study (1.0–20.0 atom%), modified TiO_2 catalysts performed better than pure

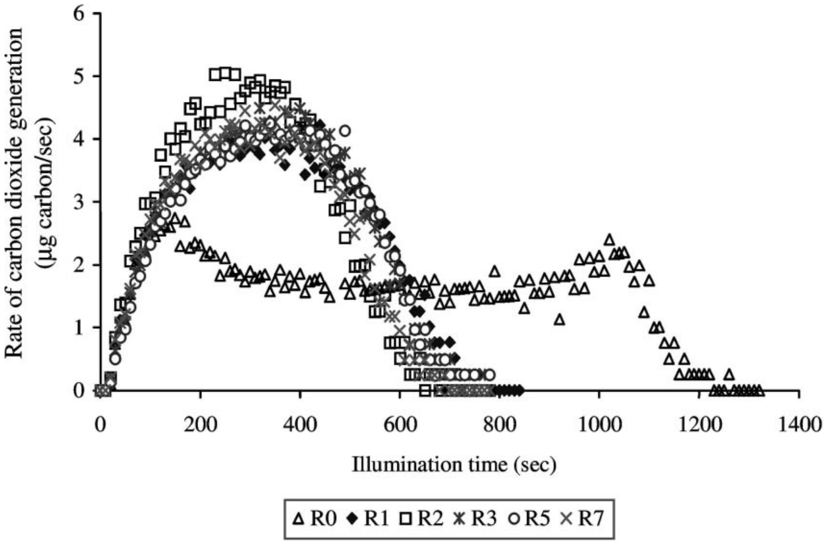


Fig. 2. Plot showing the effect of Ag^+ ions concentration on sucrose oxidation (atomic percent of Ag^+ with respect to Ti^{4+} (R) are 0, 1, 2, 3, 5, and 7, respectively).

TiO_2 in the degradation of 2000 μg C sucrose. Lee et al. [2] reported that the optimum loading of silver in TiO_2 suspensions was 1.5 atom% for the photodegradation of 1,4-dichlorobenzene. At this silver loading, the improvement in catalyst activity was approximately 35%. In this case, silver was deposited onto TiO_2 particles by the photodecomposition of silver fluoride (AgF) under a nitrogen gas atmosphere.

The photodeposition of silver under an oxygen atmosphere has been reported by several authors [2,15,18–20]. In our study, the colour of the Ag^+-modified titanium dioxide suspension changed from white to brown during illumination. Approximately, 90.6% of the initial amount of Ag^+ ions in solution was deposited on the catalyst surface at the 2.0 atom% Ag^+ loading, according to AAS analysis. The reduction of silver ions is described by Eq. (7). The reduction process enhances the photooxidation reaction since photogenerated electrons are trapped, and electron–hole recombination is reduced. Under an oxygen atmosphere, silver ions trap electrons much more efficiently than oxygen molecules [15,18], although oxygen has a higher reduction potential than silver ions in acidic media:

$$Ag^+ + e^- \leftrightarrow Ag^0 \tag{7}$$

Analysis of silver-modified particles at the 20.0 atom% loading by XRD identified the species deposited on the catalyst surface as metallic silver. The XRD patterns obtained for bare and Ag-modified Degussa P25 particles are shown in Fig. 3.

In the absence of either TiO_2 or UV illumination, the colour of the suspension remained unchanged. Hence, both the photocatalyst and light are required to reduce silver ions. Since the deposition of silver species from solution does not occur in the dark, it can be assumed that initially the Fermi level is below the onset potential for the reduction of Ag^+ ions. Under illumination, photo-generated holes are rapidly transferred to sucrose molecules in solution [21]. The photo-generated electrons may accumulate in the bulk of the TiO_2 particles or become trapped on the surface. The negative charging of TiO_2 particles implies an upward shift of the Fermi level [21]. When a critical concentration of electrons is built up in the TiO_2 particles, Ag^+ ions are reduced and deposited.

Additional experiments were conducted in order to determine whether it was the reduction of Ag^+ ions in solution to Ag metal or whether Ag deposits on the titanium dioxide surface were responsible for the enhancement in reaction rate. Ag/TiO_2 (2.0 atom% loading) particles were re-used twice for the oxidation

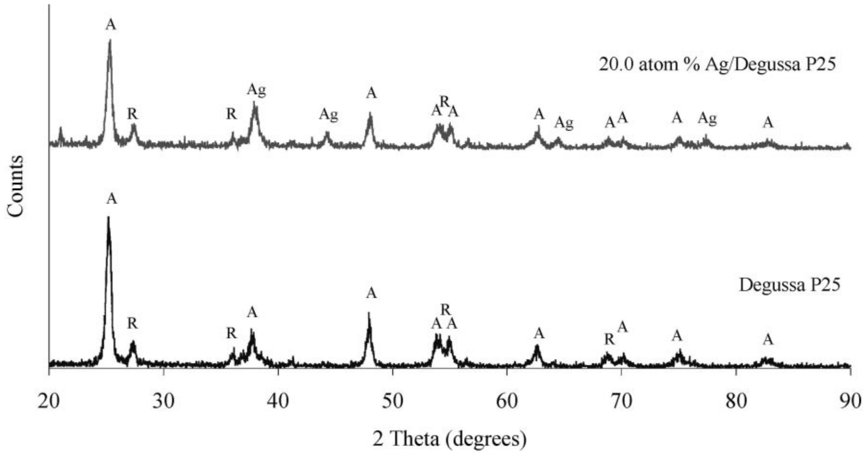


Fig. 3. XRD patterns of pure Degussa P25 particles and 20.0 atom% Ag-modified Degussa P25 particles after taking part in the photooxidation of 2000 μg C sucrose (A: anatase, R: rutile, Ag: silver).

of 2000 μg C sucrose, without the addition of new $AgNO_3$ solution into the suspension. Given that 90.6% of the initial mass of silver ions added to the suspension was reduced to form deposits on the surface, the concentration of Ag^+ remaining in solution at the end of the reaction was 5.1 ppm. The initial concentration of Ag^+ ions before deposition was 54 ppm. Hence, the modified particles were not removed from the suspension, washed and dried before re-use, since the concentration of Ag^+ ions remaining in suspension was thought to be too low to have a significant effect. This also preserves the mass loading of catalyst particles in suspension by avoiding the loss of particles during recovery. As illustrated in Fig. 4, the higher activity of Ag/TiO_2 particles can be predominantly attributed to the silver deposits on the surface, since the performance of the catalyst for the second and third sucrose additions remains approximately the same as the performance of the catalyst for the first addition of sucrose. There is a slight decrease in

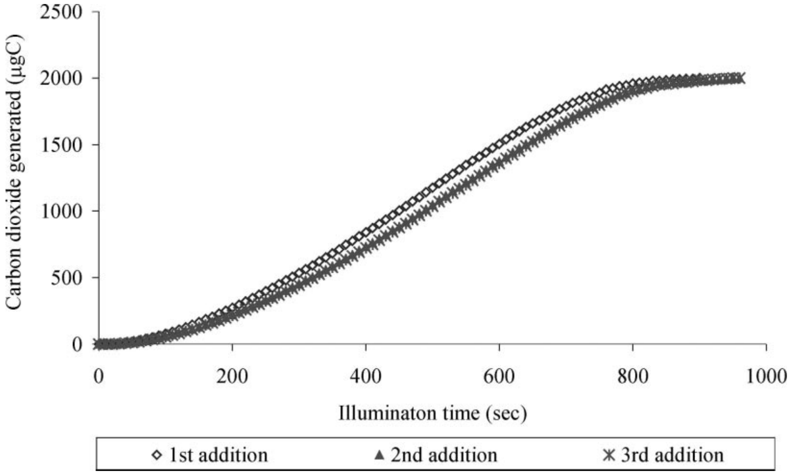


Fig. 4. Plot showing the activity of 2.0 atom% Ag-modified Degussa P25 particles being re-used in three consecutive reactions for the photooxidation of 2000 μg C sucrose.

activity between the profiles obtained for the first and second sucrose additions. Therefore the beneficial effect of electron trapping by Ag^+ ions during the reduction process cannot be neglected.

The results of the above experiment also show that the metallized TiO_2 particles are stable even after repeated use for the photooxidation of sucrose. That is, the silver deposits do not dissolve back into solution during the photooxidation reaction. To confirm this, the catalyst suspension was filtered and analysed for the concentration of silver ions in solution after the first, second and third additions of sucrose by AAS analysis. The mass of silver ions remaining as silver deposits as a percentage of the initial mass of silver ions added to the suspension after the first, second and third reactions were calculated to be 90.6, 81.9 and 86.0%, respectively. These values indicate that the silver deposits do not undergo dissolution upon illumination with near-UV light.

Researchers have also proposed that metal deposits on TiO_2 particles enhance the reaction rate by attracting electrons onto the metal particles [4,22]. This enhances the separation of photogenerated electrons and holes, leaving holes available for the oxidation of organic molecules. Another explanation for the role of deposited metal on the catalyst surface in an oxygenated system is that noble metals improve quantum yields by accelerating the removal and transfer of electrons from catalyst particles to molecular oxygen [23]. Molecular oxygen can trap photogenerated electrons to form superoxide radicals (Eq. (8)). Superoxide radicals undergo further reactions to form hydroxyl radicals via the formation of hydrogen peroxide, which are used for the oxidation of organic molecules (Eqs. (9)–(12)):

$$e^- + O_{2\,\mathrm{ads}} \rightarrow O_{2\,\mathrm{ads}}{}^{\bullet -} \tag{8}$$

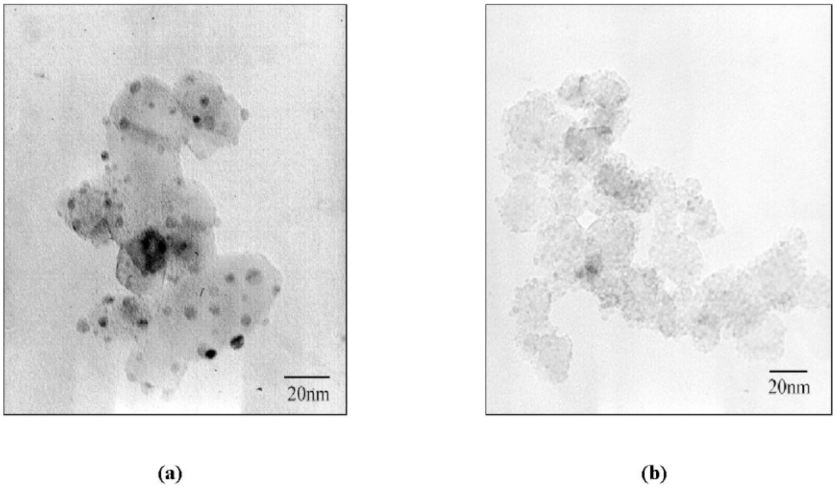
$$O_2{}^{\bullet -} + H^+ \rightarrow H_2O + HO_2{}^{\bullet} \tag{9}$$

$$HO_2{}^{\bullet} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{10}$$

$$HO_2{}^{\bullet} + HO_2{}^{\bullet} \rightarrow H_2O_2 + O_2 \tag{11}$$

$$H_2O_2 \rightarrow 2OH^{\bullet} \tag{12}$$

Light blocking by excessive silver metal deposits on titania may account for decreases in the rate of silver deposition and organic degradation [15]. Deposited silver prevents the illumination of TiO_2 particles. Hence less silver is deposited on the surface of TiO_2 particles and the consumption of photogenerated electrons decreases. Thus the rate of electron–hole recombination increases. Another reason for the drop in photoactivity in the presence of excess silver ions is the competition between reduced silver and hydroxyl ions or water molecules for photogenerated holes [12,15]. It is possible that at the optimum loading and



(a) (b)

Fig. 5. TEM micrographs of 2.0 atom% (a) and 20.0 atom% (b) Ag-modified Degussa P25 particles after use for the degradation of 100 μg C sucrose.

beyond, the rate of silver re-dissolution becomes equal to the rate of deposition [19]. Increases in the silver concentration equal to or greater than 3.0 atom% had little effect on the sucrose oxidation rate. Limiting surface concentrations of silver species on TiO_2 [20] in the presence of excess silver ions in the system is thought to be responsible for regulating the rate of sucrose mineralization.

Silver-modified Degussa P25 particles were examined under the TEM after taking part in the photooxidation of 100 μg C sucrose. Fig. 5(a) and (b) shows 2.0 and 20.0 atom% silver-modified TiO_2 particles. The silver deposits are attached to the surface of the TiO_2 crystallites. At the 20.0 atom% loading, the silver deposits give a rough appearance to the edges and surface of the TiO_2 particles. The size of the silver deposits at the 2.0 atom% loading was estimated to be 5.0 nm, while the size of the Ag particles in the 20.0 atom% Ag-modified particles is approximately 2.0 nm.

From Figs. 4 and 5, it is evident that nanoparticle sized silver deposits on the surface of titania particles have an important function in influencing the rate of sucrose mineralization. By forming sites of electrical contact between Ag deposits and the TiO_2 particles, this provides another means of reducing electron–hole recombination [24].

4. Conclusions

The addition of metal ions to Degussa P25 suspensions has been found to affect the activity of the photocatalyst for the photocatalytic oxidation of sucrose. The rate of sucrose photooxidation was enhanced in the presence of dissolved Fe^{3+} and Ag^{+} ions. From the solutions analysed, an optimum concentration of metal ions existed for both silver (2.0 atom%) and iron (1.0 atom%) ions. Beyond these concentrations, catalyst activity decreased. In the case of silver ions, the activity dropped at the 3.0 atom% Ag^{+} loading and remained unchanged as the concentration of Ag^{+} ions was increased further. However, the addition of excess Fe^{3+} ions was detrimental on catalytic activity (5.0 atom%), generating a photocatalyst with activity lower than that of pure TiO_2.

Metallic silver deposits with sizes less than 10 nm were formed on individual TiO_2 crystallites in the case of Ag-modified Degussa P25 particles. The metal deposits are believed to be responsible for enhancing the activity of TiO_2 particles in photocatalytic reactions by acting as electron sinks. This improves the separation of charge carriers.

The results of this work have several interesting outcomes. Firstly, different reaction mechanisms govern the behaviour of different metal ions in photocatalytic reactions as shown with Fe^{3+} and Ag^{+} ions as examples. Secondly, this study illustrates the use of photocatalysis for the simultaneous recovery of metal ions and photodegradation of organic pollutants in contaminated wastewaters, with the possibility of generating a more efficient catalyst. Finally, this work involves the use of metal nanoparticles in photocatalytic reactions as a means of suppressing the degree of electron–hole recombination, in order to improve the efficiency of the process.

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