An organometallic approach for the preparation of Au–TiO₂ and Au–g-C₃N₄ nanohybrids: improving the depletion of paracetamol under visible light

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Abstract

The photocatalytic degradation of paracetamol (a common analgesic also known as acetaminophen) in ultrapure water with different photocatalytic systems was performed under ultraviolet or visible irradiation. The photocatalysts employed were: commercial Degussa-P25 TiO₂ and Au–TiO₂ under UVA irradiation (365 nm) and g-C₃N₄ and Au–g-C₃N₄ under visible light irradiation (low-power (4 × 10 W) white light LEDs), improving the effectiveness of degradation rates when the gold nanoparticles (Au NPs) were combined with the semiconductors. The nanostructured photocatalysts were synthesised and characterised by transmission electron microscope (TEM), UV–vis diffuse reflectance spectroscopy and, in the case of g-C₃N₄ photocatalysts by X-ray photoelectron spectroscopy (XPS). The influence of the pH in the depletion of paracetamol with g-C₃N₄ and visible light was evaluated. In addition, the stability and lifetime of the photocatalyst g-C₃N₄ in the degradation of paracetamol were studied.

Graphical abstract

Keywords Paracetamol · Acetaminophen · TiO₂ · g-C₃N₄ · Photocatalysis · Gold nanoparticles

1 Introduction

In recent decades, myriad pharmaceuticals have been found in sewage, groundwater, surface water and drinking/tap water [1]. The occurrence of pharmaceuticals in the environment has raised a concern about their potential effects due to the fact that little is known about health effects or ecotoxicity ascribed to long-term ingestion or exposure to these kinds of emerging pollutants. Traditional wastewater treatment plants (WWTPs) are unable to remove pharmaceuticals because they were not designed for that purpose [2]. Paracetamol (also known as acetaminophen) is one of the most common and used analgesics, it has been found in aquatic environments at concentrations up to 6 ng/L [3]. Considering the potential impact of pharmaceuticals on the environment new technologies to tackle this issue have been widely investigated.

Advanced oxidation processes (AOPs) are promising oxidation treatments for the removal of these aquatic pollutants. Particularly, photocatalysis has been reported as an excellent approach to remove paracetamol [3–12]. Among the semiconductor photocatalysts, TiO_2 has been widely employed in paracetamol depletion [3–5, 7, 8] due to its strong photooxidising ability. However, some of the main drawbacks are the fast electron–hole pair recombination and the lack of visible-light activity typical of classical large bandgap semiconductors. This illustrates the urgent need for visible-light-driven photocatalysts capable of harvesting a broader range of the solar spectrum (UV light only represents 4%, whereas visible light represents 43% of the solar spectrum). In this search, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has attracted increasing attention as a novel photocatalyst due to its properties, namely: narrower bandgap than TiO_2 , facile synthesis from the abundance of inexpensive materials, good adsorption ability, high physical and chemical stability or π -conjugated structure [10, 13]. However, this promising material has some important drawbacks: (i) it might undergo fast recombination of charge carriers or (ii) it displays a narrow visible light absorption window.

A smart approach to overcome these issues consists of decorating the semiconductors with nanoparticles of plasmonic metals [9]. The nanoparticles grafted at the semiconductor surface form a heterojunction between the metal and the semiconductor called Schottky barrier. This barrier enables the transfer of the photogenerated electrons in the conduction band (CB) of the semiconductor to the plasmonic nanoparticles, leading to an effective charge carrier separation, since the nanoparticles may act as electron sinks. On the other hand, in addition to the metal–semiconductor heterojunction, the localised

surface plasmon resonance effects (LSPR), such as local heating, near-field effect or charge-transfer processes from the plasmonic nanoparticle to the CB of the semiconductor also contribute to diminish the recombination of charges [14, 16].

Among the different synthetic approaches described for the preparation of Au-TiO_2 and $\text{Au-g-C}_3\text{N}_4$ the preferred ones are photoreduction or deposition/precipitation techniques. In the case of Au-TiO_2 nanohybrids, the studies by Hidalgo et al. showed that photoreduction and chemical reduction methods are good methodologies for the preparation of Au-TiO_2 photocatalysts, which are active towards the phenol degradation [17, 18]. On the other hand, in the case of $\text{Au-g-C}_3\text{N}_4$ Di et al. reported a deposition–precipitation approach displaying higher photoactivity than similar materials prepared through impregnation/photodeposition [19]. Also, Samanta et al. described the deposition of Au nanoparticles on $\text{g-C}_3\text{N}_4$ through a deposition–precipitation method [20]. In our case, we have focused on the use of organometallic compounds as precursors for nanoparticles synthesis, which is not as common as the use of metal salts. When an organometallic complex is employed as a metal source, mild reaction conditions can be applied, avoiding the use of strong reducing agents such as NaBH_4 . This methodology allows a good control over size, shape, composition and surface state of the obtained nanoparticles. In fact, some of us have previously reported on the synthesis of mono and bimetallic gold and silver nanostructures through this approach [21–24]. In the present case, applying thermal conditions to solutions of complex $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ is enough to form colloidal nanoparticles solutions. In the case of TiO_2 the nanoparticles have to be stabilized by a polymer (PVP), but in the case of $\text{g-C}_3\text{N}_4$ the addition of ligands or polymers is not needed.

In this work, we describe a novel single-step strategy to prepare photocatalysts with enhanced visible-light activity for the removal of paracetamol by the grafting of gold nanoparticles, which are formed in situ through the controlled decomposition of an organometallic complex such as $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (tht = tetrahydrothiophene). The photodegradation of paracetamol was evaluated for different photocatalytic nanohybrids, comparing the use of a wide bandgap or a narrow bandgap semiconductor such as TiO_2 and $\text{g-C}_3\text{N}_4$, respectively. The aim of this photocatalytic study is proving the photocatalytic performance of $\text{g-C}_3\text{N}_4$ nanohybrids under less energetic irradiation conditions (visible light) compared to the effective performance achieved by TiO_2 -based nanohybrids under higher energetic irradiation conditions (UVA light). Furthermore, the efficiency of $\text{g-C}_3\text{N}_4$ under different pH conditions and its reusability and stability as a photocatalyst was evaluated.

2 Experimental

2.1 Materials

Paracetamol ($\geq 98\%$), polyvinylpyrrolidone (average mol wt 10,000) (PVP) and titanium (IV) oxide nanoparticles (Degussa P25, $\geq 99.5\%$) were purchased from Sigma-Aldrich (Germany). HPLC-grade methanol, tetrahydrofuran (THF) and absolute ethanol were purchased from Scharlab (Barcelona, Spain). Melamine (99%) and ethyleneglycol were obtained from Alfa Aesar (Germany). All chemicals were used as received without further purification. Nylon syringe filter (13 mm, 0.22 mm) were also obtained from Scharlab (Barcelona, Spain). $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ was synthesised as previously described [16].

2.2 Synthesis and characterisation of photocatalysts

2.2.1 Synthesis of photocatalysts

Commercial titanium (IV) oxide nanoparticles (Degussa P25) was employed as photocatalyst in the photodegradation of paracetamol without further treatment.

The Au– TiO_2 nanohybrid (1% in metal) photocatalyst was prepared from Au NPs and commercial TiO_2 P25. To synthesise the Au NPs, 0.125 g PVP were dissolved in 5 mL of ethyleneglycol at 80 °C under heating and stirring. 5 mg of the gold precursor $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$, were dissolved in a small amount of tetrahydrofuran (10 drops) and this mixture was injected into the former mixture at 120 °C, the reaction was magnetically stirred under reflux during 20 min. Then, the obtained colloidal solution of Au NPs was tempered and 100 mL of distilled water and 0.2156 g of TiO_2 were added. The mixture was stirred at room temperature overnight. After that, it was centrifuged and washed with distilled water several times to remove the excess of water-soluble PVP polymer.

The graphitic carbon nitride was synthesised by direct heating of melamine in a covered crucible as previously described [25, 26]. Briefly, 5 g of melamine were heated at 500 °C for 4 h followed by a second step at 520 °C for 2 h to produce a thermal-oxidative exfoliation of the material. After that, the ceramic crucible was cooled down at room temperature and the composite was crushed leading to a yellowish powder.

The Au– $\text{g-C}_3\text{N}_4$ nanohybrid (1% in metal) used as photocatalyst was prepared using the synthesised $\text{g-C}_3\text{N}_4$ and the above-mentioned Au precursor for Au NPs. 0.2156 g of $\text{g-C}_3\text{N}_4$ nanosheets were added to 5 mL of ethyleneglycol, as a solvent and co-reducing agent, and sonicated for

30 min. Then, 5 mg of the Au precursor, $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ previously dissolved in 10 drops of THF, was added to the $\text{g-C}_3\text{N}_4$ mixture and sonicated for 5 min. The mixture was magnetically stirred at 160 °C under reflux, for 15 min. The obtained nanohybrid was centrifuged and washed with ethanol. This approach takes advantage of the N-donor atoms in the triazine groups of the $\text{g-C}_3\text{N}_4$ nanosheets to effectively stabilise the in situ formed Au NPs without additional stabilising ligands, leading to naked Au NPs grafted to $\text{g-C}_3\text{N}_4$.

2.2.2 Characterisation of materials used as photocatalysts

Diffuse reflectance UV–vis spectra of pressed powder samples diluted with silica were recorded on a Shimadzu (UV-Vis-NIR 3600 spectrophotometer with a Harrick Praying Mantis accessory) and recalculated following the Kubelka–Munk function. Samples for transmission electron microscopy (TEM) were directly drop-casted from the ethanol dispersions (2–3 drops) to carbon-coated Cu grids. The TEM images were obtained with a JEOL JEM 2100 microscope. XPS experiments were performed in a Kratos AXIS Supra spectrometer, using a monochromatized Al $K\alpha$ source (1486.6 eV) operating at 12 kV and 10 mA. Wide scans were acquired at analyzer pass energy of 160 eV, whereas high-resolution narrow scans were performed at constant pass energy of 20 eV and steps of 0.1 eV. The photoelectrons were detected at a take-off angle of $F=0^\circ$ with respect to the surface normal. Basal pressure in the analysis chamber was less than 5×10^{-9} Torr. The spectra were obtained at room temperature. The binding energy (BE) scale was internally referenced to the C 1 s peak (BE for C–C = 284.9 eV).

2.3 Photodegradation procedure

For the photodegradations with visible light, a lab-made assembly consisting of four 10 W white light LED lamps (LED-Engin, CA, USA) placed equidistantly inside an 18-cm cylinder with circulating cooling water to maintain the glass reactor at a constant temperature of 25 °C was used. Figure S1 (Supplementary Material) shows the relative spectral power vs. wavelength for the LED visible lamp. The photocatalytic degradations with UV light were performed at room temperature irradiating with a UVA filtered lamp at 365 nm, 15 W (Uvitec LF-215.LS low power lamp) located 20 cm from the reactor.

In a typical degradation, 40.5 mg of the photocatalyst was added to 70 mL of a paracetamol aqueous solution (0.3 mg/L) in a Schlenk glass reactor. Before irradiation, the suspensions were sonicated for 3 min to disperse properly the photocatalyst. When the catalyst employed in the degradations consisted of $\text{g-C}_3\text{N}_4$ or Au– $\text{g-C}_3\text{N}_4$, before irradiation the dispersion was vigorously stirred for 20 min in the dark

to establish the adsorption–desorption equilibrium. During the irradiation, the mixtures were continuously stirred at 1200 rpm and aliquots of 1.5 mL were withdrawn at different times to monitor the reactions. These aliquots were previously filtered off to remove the catalyst and stored at 4 °C until analysis. The photocatalytic reactions were carried out at natural pH except in the study of the pH influence, where the paracetamol solutions were adjusted with NaOH and HCl 1 M.

On the other hand, to evaluate the reusability of the catalyst $g\text{-C}_3\text{N}_4$ eight cyclic experiments of paracetamol degradation were conducted. After each cycle, the solution was centrifuged to precipitate the catalyst and take an aliquot from the supernatant to analyse and maintain constant the amount of catalyst in each cycle. The corresponding millilitres of paracetamol solution were added to establish the initial conditions of concentration and start a new cycle.

2.4 Analytical procedure

The paracetamol concentration was measured by a high-performance liquid chromatography system: an Agilent modular 1100/1200 liquid chromatography system (Agilent Technologies, Palo Alto, CA, USA) equipped with a G1379A degasser, a G1311A HPLC quaternary pump, a G1329A autosampler and a G1315D diode array detector. A Phenomenex Luna® LC C18 100 Å (5 µm particle size, 150 mm × 4.6 mm i.d.) column was used and the mobile phase consisted of a 60% aqueous solution and 40% methanol (v/v) at a flow-rate of 1.0 mL/min. Injection volume was 20 µL and the separation was performed at room temperature. Detection wavelength was 250 nm. All samples were filtered through a nylon syringe filter before chromatographic analysis.

3 Results and discussion

3.1 Characterisation of photocatalysts

The nanohybrids were initially characterised by transmission electron microscopy (TEM) and UV–vis diffuse reflectance spectroscopy in solid state.

Figure 1 displays the solid UV–vis absorbance spectra of the samples and Figure S2 (Supplementary Material) shows the corresponding Tauc plots. The bandgap of $g\text{-C}_3\text{N}_4$ appears at lower energy than TiO_2 , 2.75 eV and 3.23 eV, respectively, this agrees with the fact that $g\text{-C}_3\text{N}_4$ absorbs lower-energy light, in the visible range. The nanomaterials Au-TiO_2 and $\text{Au-g-C}_3\text{N}_4$ present a plasmonic absorption band at 530 and 545 nm, respectively, in agreement with the presence of Au NPs. Moreover, the heterojunction between the gold nanoparticles and the semiconductors produces a

Fig. 1 Diffuse reflectance UV–vis spectra of TiO_2 P25 and Au-TiO_2 (a), $g\text{-C}_3\text{N}_4$ and $\text{Au-g-C}_3\text{N}_4$ (b)

slight decrease of the TiO_2 and $g\text{-C}_3\text{N}_4$ band gaps (2.67 eV for $g\text{-C}_3\text{N}_4$ and 3.1 eV for TiO_2) (Fig. S2).

Figure 2 shows TEM images of the synthesised photocatalysts. TEM micrographs of TiO_2 (P25) NPs displaying a size of ca. 15–30 nm or 2D-nanosheets of $g\text{-C}_3\text{N}_4$ of ca. 50–100 nm (Fig. 2a, b). The gold nanoparticles grafted on TiO_2 NPs in the material Au-TiO_2 (Fig. 2c, d) display a homogeneous distribution of spherical NPs of 4.1 ± 0.7 nm size. These nanoparticles are slightly smaller than the gold nanoparticles in the nanohybrid $\text{Au-g-C}_3\text{N}_4$, probably due to the role of PVP as stabilising polymer in the synthesis. The nanohybrid $\text{Au-g-C}_3\text{N}_4$ (Fig. 2e, f) presents spherical gold nanoparticles of 5.7 ± 1.2 nm size grafted at the surface of $g\text{-C}_3\text{N}_4$ nanosheets. Thanks to the triazine groups of the $g\text{-C}_3\text{N}_4$, which act as directing growth agent, the size of the nanoparticles in the synthesis was controlled without the need of any polymer, as was the case of the PVP in the synthesis of Au-TiO_2 nanohybrid.

Fig. 2 Representative TEM images of TiO_2 (a), $\text{g-C}_3\text{N}_4$ (b), Au-TiO_2 (c, d) and $\text{Au-g-C}_3\text{N}_4$ (e, f)

The XPS analysis of nanohybrid $\text{Au-g-C}_3\text{N}_4$ provides relevant information about the elemental composition at the surface of the materials and the oxidation states of the atoms in the nanohybrid (Fig. 3 and Table S1). The wide XPS spectrum shows the presence of the peaks corresponding to the presence of C and N as intense signals. Low-intensity peaks were attributed to O and Au atoms. The elemental composition shows that the amount of Au is 1.2% wt. It is also important to note that the amount of oxygen (1.68% wt) in $\text{Au-g-C}_3\text{N}_4$ material is twice the amount detected for pristine $\text{g-C}_3\text{N}_4$ (0.8% wt), pointing to an enrichment of oxygen species at the surface of this semiconductor arising from ethyleneglycol used as a solvent in the formation of $\text{Au-g-C}_3\text{N}_4$. A similar result was described for the microwave treatment of $\text{g-C}_3\text{N}_4$ in ethanol leading to an increased density of oxygen-containing species ($-\text{OH}$ groups) at the surface, conferring a higher hydrophilicity, better charge carrier separation and pollutant adsorption [27]. In the present case, the higher amount of hydroxyl groups in $\text{Au-g-C}_3\text{N}_4$

Fig. 3 Wide XPS spectrum for $\text{Au-g-C}_3\text{N}_4$ nanohybrid

Fig. 4 High resolution XPS spectra for C 1 s (a), N 1 s (b), O 1 s (c) and Au 4f (d) regions

Fig. 5 Photocatalytic degradation of paracetamol and absorption/desorption equilibrium with UV light (a) and visible light (b)

nanohybrid would favour the charge carrier separation but not necessarily the adsorption of paracetamol (see degradation experiments below, Fig. 5).

The high-resolution XPS spectrum for the C 1 s region shown in Fig. 4a is fitted into four peaks. An intense peak at 288.4 eV is assigned to the sp^2 carbon atoms in the triazine units of g- C_3N_4 (C–N=C), in agreement with the presence of the weak peak component of the C 1 s region at 293.9 eV assigned to double bond π -excitations. C–O bonds are related to the peak at 288.7 eV, meanwhile C–C bonds are associated with the peak at 285.2 eV. The high-resolution spectrum of the N 1 s region depicted in Fig. 4b is fitted again into four peaks. The intense peak at 398.5 eV can be associated to sp^2 N atoms in the triazine unit (C–N=C), supported by the presence of a weak peak at 404.0 eV arising from the double bond π -excitations. The weak peak at 399.6 eV is assigned to N atoms between aromatic rings in the g- C_3N_4 structure and the presence of $-NH_2$ groups is related to the peak at 401.0 eV. The assignment of the C 1 s and N 1 s regions for Au-g- C_3N_4 nanohybrid is very similar to the one obtained for pristine g- C_3N_4 (Figs. S3 and S4) and to previously reported assignments for g- C_3N_4 [28]. In addition, the high-resolution XPS spectrum for the O 1 s region (Fig. 4c) displays a peak at 532.4 eV assigned to $-OH$ groups at the semiconductor surface. This value is similar to the peak obtained for the pristine g- C_3N_4 semiconductor at 532.3 eV (see Supp. Mat.).

The high-resolution XPS spectrum for the Au 4f region is shown in Fig. 4d. The observed experimental signals can be fitted to two spin–orbit doublets equally separated in energy (ca. 3.7 eV). The most intense doublet at 83.6 eV and 87.3 eV can be assigned to metallic gold; the less intense doublet can be attributed to the presence of Au(I) oxidation state. These partially oxidized Au NPs have been recently described for Au NPs stabilised with PEG tagged imidazolium salts [29] or stabilized with the same g- C_3N_4 substrate [30]. The presence of gold atoms in positive oxidation states is attributed to a higher fraction of surface atoms with low coordination numbers when small size nanoparticles are grafted on the carbon nitride surface [31]. In addition, the assignment of the Au(I) peaks to the organometallic precursor is ruled out since the presence of fluorine atom peaks arising from the pentafluorophenyl ligands are not observed.

3.2 Photocatalytic degradation of paracetamol in ultrapure water

Figure 5 shows the results of paracetamol photocatalytic degradation in ultrapure water at natural pH with UV light and TiO_2 -based photocatalysts (Fig. 5a) and with visible light and g- C_3N_4 -based photocatalysts (Fig. 5b). All the photodegradations fit pseudo-first-order kinetics. One of the main differences is the adsorption of the pharmaceutical

on the surface of the nanocatalysts. The adsorption of paracetamol on g- C_3N_4 was 8.5% and 2% on Au-g- C_3N_4 , meanwhile the adsorption of paracetamol on TiO_2 was negligible. The surface area of commercial P25 TiO_2 NPs is 57.4 m^2/g [32], whereas the surface area of g- C_3N_4 is ca. 8 m^2/g [25]. The fact that the adsorption of paracetamol is higher when g- C_3N_4 is used would not be directly related to a larger surface area for this material because it is not the case. On the one hand, the synthetic protocol for the preparation of the Au- TiO_2 nanohybrid includes the use of PVP polymer to stabilise the formation of small size Au NPs. Although the excess of polymer is washed out, some remaining polymer would preclude a direct paracetamol-nanohybrid interaction/adsorption. In addition, a more favoured interaction between the organic functional groups of paracetamol molecule with the triazine groups of the 2D g- C_3N_4 surface would also play a significant role.

The photocatalytic reactions were carried out at a low concentration of paracetamol (0.3 mg/L). These experiments were performed at this concentration to reproduce the low levels at which the drug is frequently found in the environment. Figure 5a compares the depletion rates of paracetamol using TiO_2 and Au- TiO_2 as photocatalysts in the presence of UVA light. The degradation was slightly faster using Au- TiO_2 as a photocatalyst (0.14 min^{-1}) than using TiO_2 as photocatalyst (0.12 min^{-1}). In both cases, the kinetic constants were significantly higher than those reported for a similar catalyst in paracetamol degradations (0.0128 and 0.0160 min^{-1} for TiO_2 (P25) and 1 wt% Au- TiO_2 , respectively) with a simulated solar light (light intensity = 50.0 mW/cm^2) [33]. The nature of the irradiation sources employed in the degradations cannot be utterly comparable, however, the paracetamol depletion in this work was faster than that previously reported [33] with relatively comparable catalyst load (400–500 mg/L).

On the other hand, Fig. 5b compares the degradation of paracetamol with g- C_3N_4 and Au-g- C_3N_4 when the solutions are irradiated with visible LED light. Paracetamol was completely depleted after 24 min of irradiation using the Au-g- C_3N_4 photocatalyst and after a maximum of 50 min when g- C_3N_4 was employed. The kinetic constants for these degradations were: 0.09 and 0.17 min^{-1} for the g- C_3N_4 and Au-g- C_3N_4 , respectively. Table S2 and figure S5 (Supp. Mat.) summarise the regression parameters of the photodegradations.

The presence of the gold nanoparticles in the nanohybrids leads to the formation of a metal–semiconductor heterojunction and to a broad plasmonic absorption in the visible range. These two characteristics improved the efficiency of the photodegradations obtained for Au- TiO_2 and Au-g- C_3N_4 nanohybrids with respect to the bare semiconductors TiO_2 and g- C_3N_4 , respectively. As it was previously reported, the formation of metal–semiconductor heterojunctions increases

the photocatalytic efficiency due to several facts, namely: (i) the gold NPs can improve the electron–hole pair separation and the metal NPs act as electron sinks thanks to the Schottky barrier formed between the metal and the corresponding semiconductor; (ii) Au NPs might act as co-catalyst itself. On the other hand, the localised surface plasmon resonance (LSPR) at Au NPs improves the exciton formation in the semiconductor, induces transfer of photons to the semiconductor (optical near field enhancement) and also induces hot-electron injection from the NPs to the conduction band of the semiconductor, preventing fast electron–hole recombination and enhancing the photocatalytic activity [15, 34, 35].

Considering the intrinsic characteristics of the semiconductors used in this study and the positive improvement of their activity when Au NPs are grafted on their corresponding surfaces, we can state that both photocatalytic mechanisms lead to a fast depletion of paracetamol. Thus, when Au–TiO₂ photocatalyst and UVA are used the gold NPs can improve the electron–hole pair separation produced upon formation of photogenerated electrons in TiO₂, acting the metal NPs as electron sinks thanks to the Schottky barrier formed between the metal and the corresponding semiconductor. On the other hand, when Au–g-C₃N₄ and visible light are used both heterojunction and plasmonic effects play an important role. After visible light irradiation, a migration of photogenerated electrons in the g-C₃N₄ semiconductor towards Au NPs would take place but, at the same time, plasmonic effects such as localised heating or near-field enhancement would also assist the charge carrier separation at the semiconductor. The transfer of plasmonic hot electrons from Au NPs to the CB g-C₃N₄ would also provide a charge carrier separation at the plasmonic NPs.

3.3 Influence of pH

In the photocatalytic process, pH can have an influence on the degradation rates. Figure 6 illustrates that the depletion rates increase at acid pH and are slower at basic pH when the photocatalytic degradation of paracetamol is photocatalysed by g-C₃N₄. All degradations follow pseudo-first kinetic order with constants: 0.27, 0.091, 0.12 and 0.06 min^{−1} for pH values of 2.9, 5.9 (natural pH), 9.5 (pKa) and 11.0 pH, respectively. These results can be explained considering the surface charges of g-C₃N₄ and paracetamol. The point of zero charge (pH PZC) value of g-C₃N₄ was reported as 5.2 [36] and the dissociation constant (pKa) of paracetamol was 9.5 [9]. Under acid conditions (pH 2.9) the catalyst g-C₃N₄ is protonated and the degradation process is thermodynamically favoured. Acidification of g-C₃N₄ especially favours the photodegradation because electron–hole pair recombination is slower, which improves the charge separation in the catalyst and consequently enhances the paracetamol depletion. Moreover, this acidified g-C₃N₄, displays a higher thermodynamically driving force

Fig. 6 Influence of pH in photocatalytic degradation of paracetamol with g-C₃N₄ and visible light

for the promotion of catalytic activity [37–39]. In contrast, at basic pH (11.1) paracetamol is deprotonated and the catalyst is negatively charged generating electrostatic repulsion between g-C₃N₄ surface and paracetamol. The degradation at 5.9 and 9.5 pH, natural pH and pKa respectively, is an intermediate point between the former two cases. The degradation was not as favoured as in acidic conditions, although repulsive forces between charges of the same sign were not present. Indeed, the pH could also affect the adsorption of paracetamol onto g-C₃N₄, as can be seen in Fig. 6, the adsorption at pH 2.9 and natural pH are similar, around 8%, while at basic pH is slightly lower (4%) due to the repulsion forces.

3.4 Reusability of g-C₃N₄ in photodegradations

The stability of the photocatalyst is an important factor for its practical application. In this sense, the reusability of pristine g-C₃N₄ was evaluated for several paracetamol degradations. Figure 7 shows the rate of paracetamol degraded in several cycles after 50 min of irradiation, time that the degradation takes to complete the depletion of paracetamol in the solution with g-C₃N₄. After eight cycles the efficiency of the photocatalyst was not reduced, the catalytic activity of g-C₃N₄ in the reaction conditions is intact, at least after eight cycles. Some authors have also reported high-stability of g-C₃N₄ for six recycling runs of diclofenac [40].

4 Conclusions

In the present work, we have developed a new approach for the synthesis of gold-based photocatalysts through a fast and mild decomposition of an organometallic Au(I)

Fig. 7 Reusability of g-C₃N₄ in paracetamol photocatalytic degradation

complex such as [Au(C₆F₅)(tht)] and its grafting at the surface of NPs of the wide band-gap semiconductor TiO₂ or at the surface of 2D nanosheets of the narrow band-gap semiconductor g-C₃N₄. In the latter case, the stabilisation of small size Au NPs is achieved by the triazine groups of g-C₃N₄, what avoids the use of directing-growth polymer or ligands and leads to clean NP surfaces.

We have proved that the two different photocatalysts lead to a fast depletion of paracetamol. The Au NPs grafted on TiO₂ act as electron sinks when the photocatalyst is excited with UVA light. The Au NPs grafted on g-C₃N₄ can also act as electron sinks of photogenerated electrons in g-C₃N₄, but also plasmonic effects play an important role.

The evaluation of the activity of g-C₃N₄ at different pH conditions and its reusability towards the degradation of paracetamol indicates that this low band-gap semiconductor has a good potential for the development of practical applications using less energetic but more abundant visible light.

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Author contributions MJ-S investigation, visualization, writing—original draft. MM project administration, funding acquisition, conceptualization, supervision, writing—review and editing (catalyst synthesis and characterisation). MTT conceptualization, supervision, writing—review and editing (chromatography and kinetics).

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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