TiO$_2$, surface modified TiO$_2$ and graphene oxide-TiO$_2$ photocatalysts for degradation of water pollutants under near-UV/Vis and visible light

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HIGHLIGHTS

▶ ECT and GOT are highly active photocatalysts for DP degradation.
▶ m-TiO$_2$ photocatalyst is active for MO degradation under visible light.
▶ Photogenerated holes were identified as the main reactive species.
▶ ECT is more succeeded to generate reactive radicals from photoinduced holes.
▶ Direct oxidation with photogenerated holes is more important for m-TiO$_2$ and GOT.

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ABSTRACT

In this work the photocatalytic activity between a TiO$_2$ catalyst synthesized by a modified sol–gel method (ECT), TiO$_2$ nanoparticles surface modified with organic shell layer (m-TiO$_2$) and a graphene oxide-TiO$_2$ composite (GOT-3.3) was compared. Diphenhydramine (DP) pharmaceutical and methyl orange (MO) azo-dye were used as model water pollutants under both near-UV/Vis and visible light irradiation. The TiO$_2$ photocatalyst from Evonik Degussa Corporation (P25) was used as reference material and the pseudo-first order rate constants (k) and total organic carbon (TOC) removal were determined.

Under near-UV/Vis irradiation, the results show that ECT and GOT-3.3 are highly active photocatalysts for the degradation of DP ($k = 64.5 \times 10^{-3}$ and 62×10^{-3} min^{-1}, respectively) and mineralization (TOC removal of 55% and 50%, respectively) being the overall performance comparable to that obtained with P25 ($k = 56 \times 10^{-3}$ min^{-1} and 48% of TOC removal). The composite GOT-3.3 presents a markedly higher activity for conversion of the MO dye ($k = 126 \times 10^{-3}$, 52×10^{-3}, 49×10^{-3}, 18.1×10^{-3} min^{-1} for GOT-3.3, P25, ECT and m-TiO$_2$, respectively) as well as for its mineralization, with TOC removals tailoring the same order. Under visible light illumination, P25 is practically inactive and GOT-3.3 (for DP) and m-TiO$_2$ (for MO) are the photocatalysts with better properties than P25, or even than ECT.

Scavenger agents were used as a diagnostic tool for the analysis of the photocatalytic mechanism, being defined three ratios to understand the relevance of each step in this mechanism. Regarding DP, it was concluded that direct oxidation by photogenerated holes is more important for the modified TiO$_2$ materials (m-TiO$_2$ and GOT-3.3) than for ECT and P25 which present higher availability to generate radical species from photoinduced holes. A photoreduction mechanism on the surface of the photocatalysts was observed for MO, the addition of EDTA (electron donor) greatly enhancing the rate of MO photoreduction.

1. Introduction

Heterogeneous photocatalysis is one of the most promising advanced oxidation processes with wide applications in

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environmental remediation and solar energy conversion. Different strategies have been employed to enhance the efficiency of the photocatalytic materials, aiming lower recombination rate for the produced electron–hole pairs and narrowed band gap energy, in particular for titania (TiO₂) which is the most common photocatalyst.

In this line, the typical methods of synthesis (e.g., sol–gel, hydrothermal, solvothermal) have been optimized with the objective to tailor the TiO₂ crystalline phase and particles size [1,2]. Various approaches have been used in the literature [3] in order to extend the TiO₂ photoresponse in the visible and allow solar driven photocatalytic applications. Among the most promising, anion doping of TiO₂ [4,5] and co-sensitization of TiO₂ with inorganic or organic compounds [6] are mentioned. Alternatively TiO₂ can be combined with nanostructured carbon materials, either in core shell structures or by using single- and multi-walled carbon nanotubes [7,8], fullerenes [9,10] and graphene [11,12]. Among those graphene is recently emerging as one of the most promising to produce next generation photocatalysts [13], with excellent mobility of charge carriers, large specific surface area, flexible structure, high transparency and good electrical and thermal conduction [14].

In the present work the effectiveness of three photocatalysts (prepared by three different approaches in the frame of the Clean Water European project – GA No. 227017), and used for the degradation and mineralization of two hazardous pollutants – diphenhydramine (DP) pharmaceutical and methyl orange (MO) azo dye – under both near-UV/Vis and visible light irradiation, is compared for the first time. These photocatalysts were used at the previously optimized conditions of synthesis, namely: (i) a TiO₂ photocatalyst (ECT) prepared by a modified sol–gel method [1]; (ii) a surface modified nanoparticulate titania (m-TiO₂) photocatalyst with visible light activity [15]; and (iii) a graphene oxide-TiO₂ composite (GOT-3.3) synthetized by liquid phase deposition [16]. The possible pathways for photocatalytic degradation were examined through the use of scavengers for both radicals and holes (t-BuOH and EDTA, respectively), and three different ratios were defined to illustrate the significance of each step in the photodegradation mechanism, namely: (1) oxidation by reactive radicals formed from photoexcited electrons; (2) direct oxidation by photogenerated holes; and (3) oxidation by reactive radicals formed from photoinduced holes.

2. Experimental

2.1. Reagents and materials

High-purity analytical grade diphenhydramine (DP, 99%), methyl orange (MO, 99%) and tert-butanol (t-BuOH, ⩾99.7%) were obtained from Sigma–Aldrich and ethylenediaminetetraacetic acid (EDTA, >99%) from Fisher Scientific. Acetonitrile (⩾99.8%) was used with HPLC grade (Chromanorm). Ammonium hexafluorotitanate (>99.99%), boric acid (>99%), titanium butoxide (97.0%) and tetrabutyl titanate (97.0%) were obtained from Sigma–Aldrich. Ethanol (99.5%), citric acid (99.5%) and urea (25% w/v) were supplied by Panreac.

2.2. Catalysts synthesis and characterization

ECT-1023t (referred in the present work as ECT) was synthesized following a sol–gel procedure (using titanium butoxide as precursor) and a calcination temperature of 750 °C which allows tailoring the optimal size, crystallinity and surface area of TiO₂ particles. Modified TiO₂ (m-TiO₂) nanoparticles, that already proved enhanced photocatalytic activity under visible light irradiation

[15], were synthesized by hydrolysis condensation of tetrabutyl titanate following combustion with urea, at a calcination temperature of 450 °C. GOT-3.3-200 (referred in the present work as GOT-3.3) was prepared by liquid phase deposition (using ammonium hexafluorotitanate as precursor) with an optimal graphene oxide content of 3.3 wt.% and 200 °C as temperature of treatment. These three materials were fully characterized elsewhere [1,15,16], some of the most characteristic information is shown in Table 1. The TiO₂ photocatalyst from Evonik Degussa Corporation (P25) was used as reference material.

2.3. Photocatalytic experiments

The photocatalytic degradation of DP (3.40×10^{-4} mol L^{-1}) or MO (3.05×10^{-5} mol L^{-1}) was carried out at room temperature (25 °C) in aqueous solutions under near-UV/Vis and visible light irradiation. The experiments were performed in a quartz cylindrical reactor filled with 7.5 mL of the selected model pollutant, as described elsewhere [16]. Briefly, a Heraeus TQ 150 medium-pressure mercury vapor lamp was used as irradiation source delivering near-UV/Vis irradiation ($\lambda > 350$ nm; 50 mW cm^{-2}) and for visible light experiments a cut-off long pass filter was used ($\lambda > 430$ nm; 6 mW cm^{-2}). Before turning on the lamp, the suspensions were saturated with an oxygen flow and magnetically stirred for 30 min to establish an adsorption–desorption equilibrium. The optimal catalyst load was established in preliminary photocatalytic experiments with the aim to avoid the ineffective excess of catalyst (1.0 g L^{-1} and 0.5 g L^{-1} for DP and MO, respectively). Experiments in the absence of catalyst were also performed to determine the contribution from direct photolysis. The optimal operating pH values used for the photocatalytic runs (4.4 for MO and natural pH of 5.9 for DP) were selected in preliminary experiments performed at different pH values, both pollutants being present in their protonated form at such conditions.

The concentration of DP was measured by HPLC with a Hitachi Elite LaChrom system equipped with a Hydrosphere C18 column. The concentration of MO was determined by UV–Vis spectrophotometry at the characteristic wavelength reported in literature of 464 nm [3], by using a Jasco V-560 spectrophotometer. The total organic carbon (TOC) was also determined for selected samples using a Shimadzu TOC-5000A analyzer. Trapping experiments of holes and radicals were performed by adding excess of EDTA or t-BuOH, respectively.

The photocatalytic oxidation of the tested pollutants can be ascribed to a pseudo-first order kinetic model, as described by the following equation:

$$C = C_0 e^{-kt} \tag{1}$$

where C corresponds to pollutant concentration, k is the pseudo-first order kinetic constant, t is the reaction time and C_0 is the pollutant concentration for $t = 0$. The values of k were obtained by non-linear regression. Table 2 shows the k constants (with respective standard errors) obtained by fitting the model described in Eq. (1), the coefficient of variation, CV, expressed in percentage as k_{CV}

Table 1
Characterization of catalysts.

Catalyst	S_{BET} (m² g⁻¹)	Crystalline phase (%)[a]	Particle size (nm)[a]	E_g (eV)
P25	52	80 (A)/20 (R)	22 (A)/25 (R)	3.18
ECT	18	89–94 (A)/11–6 (R)	57 (A)/86 (R)	2.97
m-TiO₂	141	100 (A)	8 (A)	2.28
GOT-3.3	117	100 (A)	4 (A)	2.95

[a] A: anatase; R: rutile.