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Degradation of organophosphorus flame retardant tris (1-chloro-2-propyl) phosphate (TCPP) by visible light N,S-codoped TiO_2 photocatalysts

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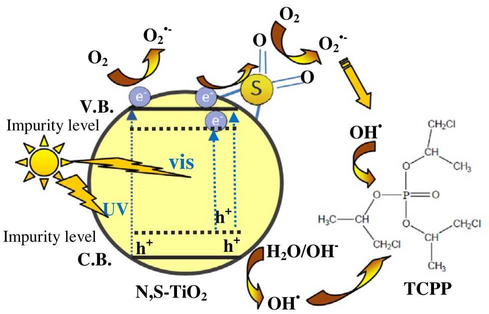
HIGHLIGHTS

- N,S-doped TiO_2 photocatalysts have been prepared by sol–gel.
- N,S-TiO_2 catalysts showed low crystallite sizes and visible-light response.
- Photocatalytic activity was evaluated towards TCPP degradation in aqueous solutions.
- N-doped TiO_2 was found the most photoactive catalyst under UV–vis light.
- N,S-TiO_2 with equimolar Ti:N,S ratio showed the higher activity under visible light.

GRAPHICAL ABSTRACT



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ABSTRACT

N and N,S co-doped TiO_2 catalysts were prepared by a simple sol–gel method and were characterized by various techniques such as X-ray diffraction, scanning electron microscopy, UV–vis spectroscopy, porosimetry and particle size distribution. The photocatalytic efficiency of the prepared catalysts was evaluated for the degradation of organophosphorus flame retardant TCPP in aqueous solutions at environmental relevant concentrations under UV–vis and visible light irradiation. All the prepared N and N,S doped catalysts showed lowered crystallite size and higher visible-light response compared to the undoped TiO_2 catalyst. An increased surface acidity was observed for N,S co-doped catalysts as a result of surface sulfate species which play a crucial role in the photocatalytic performance. N-doped TiO_2 was found to be the most photoactive catalyst for the removal of TCPP, under UV–vis irradiation. Among N,S co-doped TiO_2 catalysts, the one prepared with equimolar Ti:N,S ratio showed the higher performance for the removal of TCPP under both UV–vis and visible irradiation. Its higher activity was attributed to the higher surface area, larger pore volume, well-crystallized anatase and red shift in light absorption. Under visible light irradiation the degradation kinetics of TCPP were slower than under UV–vis irradiation due probably to reduced production of hydroxyl radicals.

1. Introduction

Over the past decades, TiO_2 has been widely used to treat water pollutants due to its low cost, good stability and high photocatalytic activity [1]. In recent years, much effort has been devoted

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at the production of efficient and visible-light responsive TiO_2 [2]. A variety of approaches have been attempted to extend TiO_2 photocatalytic function under visible light [2,3]. Doping with metal [4] or nonmetal [5] elements has proved to be one of the most effective methods to increase semiconductor's hole-electron separation rate and visible light response by creating new energy levels between the conduction and valence bands [5,6].

Anion doping with p-block elements [6] such as N [7], S [8], C [9], F [10], I [11] and B [12] has been largely employed to sensitize TiO_2 toward visible light. However, the insertion of dopant impurities into the oxide structure may also increase the rate of the undesired recombination of photocatalytically generated charge carriers [6], thus the effectiveness and the nature of doping is still a matter of investigation. Among nonmetal doping the most widely used is N-doping. Nitrogen can be easily introduced in the TiO_2 structure, due to its comparable atomic size with oxygen, small ionization energy and high stability. Due to the easy incorporation of nitrogen ions into TiO_2 lattice, co-doping with nitrogen and one other nonmetal such as F (N,F co-doping) [13], S (N,S co-doping) [14], I (N,I co-doping) [15], C (N,C co-doping) [16] and B (N,B co-doping) [17] has been investigated in order to maximize the benefits of nitrogen incorporation.

N,S co-doping [14,18–28] has been attracted the interest of many investigators during the last few years. In the majority of the reports [14,18–24] dealing with N,S co-doped catalysts, thiourea was used as N and S dopants source. In the more recent reports [14,24] the final modified TiO_2 powders were referred as N, S and C co-doped. This means that when thiourea was used as N and S precursor in a usual sol – gel process, carbon contained into thiourea or other used solvents leads into C-doped TiO_2 states. As a result the use of different N and S dopant sources such as $(NH_2)_2CO$ and $(NH_2)_2SC$ salts, was investigated by other research groups [25,26]. The alternative use of N,S co-doped TiO_2 materials as photocatalytic anode electrode [27] and solar cells [28] has also been studied.

Regarding the application of semiconductor photocatalysis for the degradation of environmental pollutants, numerous dyes, phenols (substituted or not), pesticides and pharmaceuticals have been mainly used as probe molecules. However, applications for another important emerging pollutant's category like flame retardants have been investigated in a lesser extent. The existing studies are focused mainly on tetrabromobisphenol A and other polybrominated diphenyl ethers (PBDEs) [29–33] whereas for organophosphorus flame retardants (OPFRs), which have replaced the banned PBDEs, the data are very scarce [34]. OPFRs are extensively used in various different applications [35,36] and they can migrate from the host materials into surrounding environmental media relatively easily by volatilization, leaching and/or abrasion due to the non-chemically bonded incorporation for many of them in the material matrices [36]. In addition, most of them presented high persistence [37] and consequently widely distribution in all environmental compartments [36], being considered as emerging contaminants. Finally, several OPFRs are known to exert toxic effects (e.g. neurotoxicity, carcinogenicity, endocrine disruption) and additionally, the more lipophilic OPs have the potential to bioaccumulate [36–38].

Among OPFRs, the focus in the present study is given on tris (1-chloro-2-propyl) phosphate (TCPP) due to: (a) the high persistence of the halogenated OPFRs in the environment [37,39]; (b) the high release of TCPP from finished products, i.e. approximately 40% [40], and (c) the heavy production and wide applications of TCPP rendering it as an EU high production volume (HPV) chemical which is also included in the European Commission fourth priority list [41]. TCPP represents approximately 80% of the chlorinated OPFRs in Europe and is by volume the most important OPFR [42]. Recent studies have reported that TCPP is among the most frequently detected emerging pollutants in wastewater effluents in EU at concentrations as high as 24 $\mu g\ L^{-1}$ [42] due to incomplete removal by conventional wastewater treatment plants (WWTPs) [43,44]. TCPP has been also detected in surface water, ground water and drinking water samples reaching concentrations ranging from few $ng\ L^{-1}$ to few $\mu g\ L^{-1}$ [36,45–47].

In previous reports of Giannakas et al. N,F co-doped [13], N,I co-doped [15] and B,N,F tri-doped [17] TiO_2 were successfully prepared via an impregnation method using salts as N, I, F and B dopant and showed improved performance towards the simultaneous photocatalytic oxidation of benzoic acid and photocatalytic reduction of Cr(VI). On the other hand, the photocatalytic degradation of TCPP by using standard P25 TiO_2 photocatalyst was recently investigated by Antonopoulou et al. [34]. In this study, a simple preparation method for N,S co-doped TiO_2 photocatalysts using $(NH_4)_2SO_4$ salt as N,S dopant source in order to avoid C-doped TiO_2 state as well as the characterization of the obtained photocatalysts by various techniques are presented. Thus, the present work specifically aims to: [i] prepare and characterize visible-light active N,S co-doped TiO_2 photocatalysts; [ii] evaluate the optimum Ti to N,S molar ratio for the optimum photoactivity of the photocatalysts, and [iii] evaluate the photocatalytic performance of the prepared catalysts towards TCPP oxidation at environmental relevant concentration levels.

2. Experimental

2.1. Chemicals

TCPP (mixture of isomers) analytical standard was obtained by Sigma-Aldrich (USA). LC-MS-grade solvents (acetonitrile, isopropanol, methanol and water) were supplied by Merck and used for UPLC-TOF-MS analyses. Titanium (IV) butoxide and $(NH_4)_2SO_4$ used for the preparation of catalysts were purchased from Sigma Aldrich. Sodium azide (NaN_3) and *p*-benzoquinone were obtained from Sigma-Aldrich. In order to remove the TiO_2 particles of the solution samples during the photocatalytic experiments, membrane 0.45 μm filters were supplied by Millipore (Bedford, USA).

2.2. Preparation of materials

The preparation method was based on a simple sol – gel impregnation method [13,15,17]. For the preparation of the N,S co-doped materials 3.4 mL titanium (IV) n-butoxide was added drop wise to 50 mL aqueous $(NH_4)_2SO_4$ solution at given concentrations under vigorous stirring. Three different concentrations of $(NH_4)_2SO_4$ were used in order to have final [N,S:Ti] molar ratio 0.5, 1 and 1.5 respectively. The milky suspension obtained was aged for 24 h at room temperature (25 °C) and subsequently dried at 120 °C for at least 48 h. The obtained xerogels were calcined at 500 °C in air for 1 h with a ramp rate 5 °C/min and thereafter were dispersed in water. The obtained suspensions were sonicated for 2 h in a sonication bath, filtrated and washed with distilled water in order to remove impurities. Finally, the as-prepared catalysts were dried again at 120 °C and ground in agate mortar. N-doped TiO_2 were also prepared by using NH_4Cl as dopant precursor, using a similar procedure. The chosen optimum N:Ti molar ratio was equal to unit as previously reported [13]. Overall, we have prepared three N,S co-doped catalysts herein named as TNS0.5, TNS1, TNS1.5, and one N-doped solid herein named TN1 for comparison purposes. In addition, undoped TiO_2 was prepared with the same method. The full details of the chemical conditions used for each sample, are listed in Table 1.