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Effect of dopants on the structure of titanium oxide used as a photocatalyst for the removal of emergent contaminants

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ABSTRACT

Photocatalysts composed of titanium dioxide modified with B, F, N and P have been synthesized, characterized and applied to the degradation of caffeine, diclofenac, ibuprofen and salicylic acid. The modified TiO_2 samples were prepared by the sol–gel technique starting from titanium(IV) isopropoxide and using H_3BO_3, NH_4F, $N(C_2H_5OH)_3$ and H_3PO_4 as precursors of the modifiers, with the content varying between 0 and 5 wt%. Structural characterization was based on nitrogen physisorption at −196 °C, powder X-ray diffraction (PXRD), simultaneous thermogravimetric/differential thermal analysis (TG/DTA) and X-ray photoelectron spectroscopy (XPS). The structural properties of the modified TiO_2 solids were significantly different depending on the nature and amount of modifiers and the calcination temperature. TiO_2 in the anatase phase was obtained in all cases and was stable upon calcination at 400 °C. The photocatalytic degradation of caffeine, diclofenac, ibuprofen and salicylic acid by modified TiO_2 was investigated under ultraviolet irradiation at 25 °C. The photocatalytic degradation behavior followed the order: caffeine > diclofenac = ibuprofen > salicylic acid. B-doped TiO_2 was the most efficient catalyst in the degradation of these selected emerging contaminants.

Introduction

Advanced oxidation processes (AOPs) include all the processes based on *in situ* generation of strong oxidation radicals capable of degrading and eliminating contaminants in water; for instance, Fenton oxidation, ozonation, photocatalysis and their combinations. Photocatalysis has attracted considerable attention in recent years and has been extensively studied because with this technology, additional chemical compounds, such as oxidants, are not added to the environment [1,2]. Photocatalysis is particularly suitable for the treatment of low water volumes with a low concentration of organic contaminants and is based on a solid semiconductor with the ability to be excited by photons with energy larger than its band gap, thus creating electron–hole pairs. These charges can migrate to the surface of the semiconductor photocatalyst yielding radical species that can react with organic molecules by means of redox reactions [1–3].

The use of semiconductor photocatalysts such as SnO_2, TiO_2, WO_3, ZnO and ZnS for applications in environmental remediation [2], H_2 production [4] and CO_2 reduction [5] has been reported in recent years. TiO_2 has attracted considerable interest in recent decades due to its electronic and surface acid–base properties, low toxicity and low cost. In order to improve its photocatalytic efficiency for water treatment, TiO_2 requires some modifications on its surface and electronic properties to facilitate the redox reactions. In this respect, several strategies have been reported to improve TiO_2 performance, including morphological and chemical modifications. The morphological approaches are based on controlling the particle size and creating a suitable porous structure. Thus, great efforts have been focused on designing enhanced photocatalysts by supporting nanostructured TiO_2 on porous solids with a large specific surface area, as thin films on substrates or synthesizing titania nanostructures [6–14]. Chemical approaches include metal or non-metal ion doping [15,16], inorganic complexing or organic dye sensitization and semiconductor heterojunctions by coupling with other semiconductors

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[17–19]. Among these doping elements, substitution for *p*-block elements (B, C, N, F, S, P and I), either at the Ti^{4+} or O^{2-} sites, has been explored as a way to enhance titania photoefficiency [20–23].

Emerging pollutants can be defined as a new class of chemicals not currently subjected to any discharge limitations or regulatory status whose effects on human health and the environment are not still sufficiently known. This type of compounds includes drugs, pharmaceutical products, pesticides, herbicides, personal care products and endocrine-disrupting complexes [24]. These contaminants are excreted unmetabolized and accumulate in the aquatic environment because of the inability of conventional wastewater treatment plants to degrade them [25]. Considering their potential impact, various management and treatment methods can be applied to reduce the concentration of these emerging contaminants. Many current efforts focus on developing new technologies for wastewater treatment and the production of drinking water. Among these emerging pollutants, non-steroidal anti-inflammatory drugs (NSAIDs), commonly available and used in non-prescription medication, are often present in surface water.

All the drugs considered in the present study (see Fig. S1) are widely used and frequently found in wastewater. Caffeine is an alkaloid belonging to the methylxanthine family. Despite humans most commonly consume caffeine in infusions. It is a central nervous system stimulant and can cause a condition of wakefulness and increased mental activity. Caffeine facilitates the performance of muscular work and is frequently included in oral analgesic preparations with aspirin, paracetamol or codeine; however, its clinical benefit is under debate. Diclofenac is a NSAID mainly used as its sodium salt for the relief of pain and inflammation of different origin and after some surgical procedures. Ibuprofen, is also a NSAID, but has weaker anti-inflammatory properties than other NSAIDs. It is widely used in the management of mild to moderate pain and inflammation, as well as to reduce fever. Salicylic acid is naturally found in the willow tree and it is an important active metabolite of aspirin. Salicylic acid has keratolytic properties and also possesses fungicidal properties and is used topically in the treatment of dermatophyte skin infections [26].

This study was targeted to the preparation and study of the structural properties of materials resulting from the combination of titanium dioxide with different amounts of non-metallic dopants, namely, B, F, N and P. These materials were used as efficient photocatalysts for the removal of widely used emerging pollutants such as caffeine, diclofenac, ibuprofen and salicylic acid.

Experimental

Materials

Materials and reagents used for the synthesis of modified TiO_2 were: titanium(IV) isopropoxide (>97%), 2-propanol (>99%), hydrochloric acid (HCl, 37%), boric acid (H_3BO_3, 99.97%), ammonium fluoride (NH_4F, 99.99%), triethanolamine ($N(C_2H_4OH)_3$, 98%), phosphoric acid (H_3PO_4, 99.999%). Caffeine (CA, 1,3,7–trimethylxanthine), diclofenac (DF, 2-[2-(2,6-dichloroanilino)phenyl]acetic acid), ibuprofen (IB, (RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid, >98%) and salicylic acid (SA, 2-hydroxybenzoic acid, >99%) were used without any purification. Two commercial forms of titanium oxide (anatase and rutile) were used as reference catalysts. HCl was supplied by Acros, and all the other reagents, as well as anatase and rutile, were supplied by Sigma-Aldrich.

Preparation of modified TiO_2

Modified titanium oxide samples were synthesized by the sol–gel method using the following procedure [27–33]: a solution (A) was prepared by dissolving 1 cm^3 of HCl (1.5 mol/dm^3) and the corresponding amount of the doping agent (H_3BO_3, NH_4F, $N(C_2H_4OH)_3$, H_3PO_4) for a given mass percentage in the final solid (0.1, 0.5 and 5 wt%) in 20 cm^3 of 2-propanol. A second solution (B) was prepared by dissolving 5 cm^3 of Ti-isopropoxide in 20 cm^3 of 2-propanol. Solution A was dropwise added to solution B under constant magnetic stirring for 30 min. The solvent was removed at 60 °C for 16 h until a dried white powder was obtained, which was then calcined at 200, 300 or 400 °C for 4 h to obtain the final solids by removing the water adsorbed by the solids during the synthesis and the precursors used to incorporate the doping elements. A similar method was followed for preparing unmodified titanium oxide (without the addition of modifiers) used as a blank reference. The catalysts were named according to the dopant used and its content; for instance, TiO_2 (undoped TiO_2), TiB0.1 (TiO_2 doped with 0.1 wt% B) and TiF0.5 (TiO_2 doped with 0.5 wt% F). When needed, the calcination temperature of the solid (in °C) was added at the end of the name.

Characterization techniques

The catalysts were characterized by several techniques. Powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-5000 diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 0.1548$ nm). The working conditions used were 30 mA, 40 kV and a scanning rate of 2° (2θ)/min from 10 to 100°. Thermal analyses were performed in a Hi-Res TGA2950 apparatus from TA-Instruments; the measurements were carried out at a heating rate of 10 °C/min from room temperature to 900 °C under air dynamic atmosphere (60 cm^3/min). Nitrogen (Air Liquide, 99.999%) adsorption was carried out at −196 °C using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). Prior to the adsorption measurements, the samples were degassed *in situ* under vacuum (residual pressure less than 0.1 Pa) for 24 h at 200 °C. The photoelectron spectra were recorded with a SPECS Phoibos 150 1D-DLD spectrometer equipped with an Al Kα (1486.7 eV) X-ray source. The C 1 s signal at 284.6 eV was used as reference for peak energy calibration. The spectra were fitted to the respective element signal using the CasaXPS software (Casa Software Ltd, UK). Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

Evaluation of the photocatalytic performance

The photocatalytic behavior of TiO_2 and modified TiO_2 solids under ultraviolet (UV) light was estimated by measuring the concentration of the organic molecules in aqueous solution (ultrapure water obtained from Milli-Q equipment, Millipore). Blind tests before the photocatalytic runs in the absence of a catalyst (photolysis test) or illumination (adsorption test) were also carried out.

The catalytic experiments were carried out on a 1.0 dm^3 cylindrical glass photoreactor batch with a medium-pressure Hg lamp TQ 150Z1 (UV-Consulting Peschl, Spain) immersed in a quartz sleeve placed in the middle of the reactor surrounded by a water cooling jacket (PolyScience Digital Temperature) to maintain a constant temperature (25 °C). Magnetic stirring (700 rpm) was used for proper mixing and the whole process was carried out in a photon cabinet. First, 0.7 dm^3 of the solution of the organic molecule (CA, DF, IB, or SA) in water, with a concentration between 1 and 15 mg/dm^3, was mixed in the photoreactor with the catalyst at a concentration between 100 and 1000 $mg_{catalyst}$/dm^3. After 40 min of premixing at 25 °C, photocatalytic degradation was initiated by switching on the UV lamp. The suspension was sampled at established time intervals, and filtered (Durapore membrane filters, 0.45 μm) to remove the catalyst powder and to

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