ARTICLE IN PRESS

Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Concurrent role of metal (Sn, Zn) and N species in enhancing the photocatalytic activity of TiO_2 under solar light

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ARTICLE INFO

Keywords:
N-doped TiO_2 photocatalyst
Sn/Zn guest species
Tetracycline
ESI–MS
Photodegradation pathways
ζ-potential

ABSTRACT

TiO_2 modification by both non-metal and metal species is a popular strategy to promote the semiconductor visible light absorption and photocatalytic performance. In this work, tin and zinc are compared as metal promoters to enhance the photocatalytic activity of N-doped TiO_2 under solar light. The synthesized samples were tested under both UV and simulated solar irradiation toward the photocatalytic degradation of tetracycline, an emerging water pollutant. All copromoted samples (N + Sn and N + Zn) revealed higher efficiency under solar light in the mineralization of the pollutant with respect to both the pristine and N-doped ones. The enhanced photocatalytic efficiency of these samples was traced back to the modifications introduced by the different guest species to the structural (X-ray Powder Diffraction, XRPD), morphological (High-Resolution Transmission Electron Microscopy, HR-TEM and Brunauer-Emmett-Teller analysis, BET), spectroscopic (X-ray Photoelectron Spectroscopy, XPS, Energy Dispersive X-ray Spectroscopy, EDX and Diffuse Reflectance Spectroscopy, DRS) and surface features (ζ-potential). In this regard, the increased surface area, the modifications of the phase composition and the enhanced visible light harvesting seem to play a pivotal role in affecting the photocatalytic performance. Mass spectrometry analyses allowed us to identify several reaction intermediates and propose different degradation mechanisms depending on the type of metal promoter.

1. Introduction

Titanium dioxide (TiO_2) is probably the most widely adopted photocatalyst, due to its chemical and thermal stability, low cost, non-toxicity and high efficiency under UV irradiation. However, its wide band gap (≥ 3.0 eV) prevents the use of visible light to activate the semiconductor. Non-metal species have been extensively adopted in order to enhance its visible light harvesting. Among these elements, starting from the pioneering work of Asahi et al. [1], nitrogen has been the focus of extensive research as it proved able to promote visible light absorption. Nonetheless, the introduction of N as guest species in the TiO_2 lattice generates localized intra gap states that can promote electron/hole recombination phenomena, thus decreasing the photocatalytic efficiency [2].

A viable strategy to improve the photocatalytic activity of N-doped TiO_2 is the development of mixed oxide structures and heterojunctions able to limit recombination phenomena by enhancing the charge separation [3,4]. Due to their band structure, SnO_2 and ZnO have been frequently adopted to develop SnO_2/TiO_2 and ZnO/TiO_2 heterojunctions [5–12], although reports of the formation of heterojunctions with N-doped TiO_2 have been much more scarce.

Codoping of TiO_2 with nitrogen and a metal species has also emerged as a promising strategy to boost the photocatalytic efficiency of N-doped materials. Several transition elements have been reported as efficient codopants of N-doped TiO_2 [13–15], leading in some cases to synergistic effects in the visible light absorption [16,17]. Few articles can be found in the literature regarding codoping of TiO_2 with N and Zn or Sn [18]. Zhuang et al. reported an enhanced activity of Sn and N-codoped TiO_2 systems with respect to both photocatalytic hydrogen evolution and Rhodamine B degradation [19]. Kaur et al., studying a series of metal, N codoped titania systems, suggested Zn as an efficient species able to promote photocatalysis reducing the recombination centres [20]. The improved photocatalytic activity of Zn, N-codoped TiO_2 was confirmed by Hu et al. for samples prepared by nitridation and hydrogenation with high oxygen vacancies content [21].

In the present work, the modifications provided by Sn and Zn

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https://doi.org/10.1016/j.cattod.2017.12.017
Received 8 August 2017; Received in revised form 1 November 2017; Accepted 16 December 2017

Please cite this article as: Rimoldi, L., Catalysis Today (2017), https://doi.org/10.1016/j.cattod.2017.12.017

species on the physicochemical features and the photocatalytic activity of N-doped TiO_2 systems was studied. High metal contents were investigated to favour the occurrence of partial segregation of the metal oxides. The obtained samples were characterized from the structural, morphological, optical and spectroscopic point of view. Their photocatalytic activity was tested both under UV and simulated solar irradiation toward the degradation of tetracycline (TC), an emerging organic pollutant belonging to the class of pharmaceutics and personal care products (PPCPs). To the authors' best knowledge, for the first time, differences in the photocatalytic degradation mechanism of Sn- and Zn-modified titania samples were identified and related to the modifications of the physicochemical features induced by metal species.

2. Experimental section

2.1. Sample preparation

Reactants were purchased from Sigma-Aldrich and used without further purification. Solutions and suspensions were prepared with doubly-distilled water, passed through a Milli-Q apparatus.

In a typical synthesis, carried out at 60 °C, 10.7 g of titanium(IV) isopropoxide and 11.3 g of 2-propanol were mixed for 15 min. In the case of the metal modified samples, the required amount of $SnCl_4 \cdot 5H_2O$ or $ZnCl_2$ was dissolved in the mixture. Successively, 65 mL of either NH_4OH (N/Ti molar ratio = 0.5) or KOH aqueous solution for N-doped and undoped samples, respectively, was added drop-by-drop while stirring vigorously (300 rpm). In both cases, the base solution concentration was adjusted in order to obtain a final pH of 9. The reaction mixture was then stirred for 90 min to complete the hydrolysis. The resulting precipitate was washed three times by centrifugation-resuspension cycles and later dried at 80 °C overnight. Finally, the xerogel was calcined at 400 °C for 6 h under oxygen flux (9 NL h^{-1}). TiO_2 samples were labelled as Ti, TiN, TiNSnx, and TiNZnx for undoped, N-doped and N,metal co-promoted samples, respectively, where *x* identifies the metal/Ti molar ratio (5 or 20%).

2.2. Materials characterization

The adopted material characterizations are detailed in the Supplementary Material.

2.3. Photocatalytic tests

All samples were tested toward the photocatalytic degradation of tetracycline hydrochloride in water under both UV (Jelosil HG500 lamp; effective irradiation power: 30 mW cm^{-2}) and simulated solar light (Lot Oriel halogen lamp; effective irradiation power: 7.5 mW cm^{-2}) irradiation. Photocatalytic experiments were performed at 20 °C in a 300-mL jacketed reactor using an initial TC concentration of 35 mg L^{-1} and a photocatalyst concentration of 0.5 g L^{-1}. An oxygen flux (9 NL h^{-1}) was bubbled in the reactor during the photocatalytic experiments. Both the TC disappearance and the mineralization degree were monitored as described previously [22]. Before light irradiation, samples were left in the dark for 30 min in order to reach the adsorption equilibrium. Photolysis tests were also conducted to quantify the molecule degradation in the absence of photocatalyst, leading to less than 5% mineralization. Initial kinetic constants (pseudo-first order) were calculated within 35 min and 120 min of irradiation in the case of UV and solar irradiation, respectively.

The reaction intermediates were also investigated by electrospray ionization mass spectrometry (ESI–MS) using a LCQ Advantage system (Thermo Finnigan) MS spectrometer, equipped with an electrospray ionization source and an 'Ion Trap' mass analyser. Sample solutions were analyzed by direct infusion, applying +3.0 kV at the capillary entrance and using a drying gas at 350 °C. Full-scan MS spectra were acquired in the 150–1000 mass/charge (*m/z*) range.

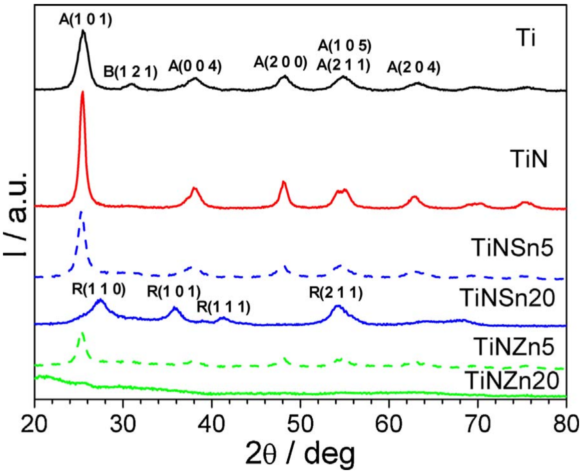

Fig. 1. XRPD patterns of the synthesized samples. The main peaks of the three TiO_2 phases (A: anatase, B: brookite, R: rutile) are highlighted.

3. Results and discussion

3.1. Materials characterization

Fig. 1 reports the XRPD patterns of the investigated samples. Sharp differences in terms of phase composition and average crystallite size are appreciable depending on the nature and nominal amount of the guest species (Table 1). The undoped sample is an anatase-brookite composite in a *ca.* 2:1 ratio, as clearly appreciable from the presence of the brookite (121) reflection. N-doping promotes the anatase content (space group: *I4₁/amd*; tetragonal structure) and crystal growth (Table 1), in agreement with previous reports about N-doped TiO_2 [23,24].

The presence of Sn seems instead to result in lower crystallinity and anatase content with respect to TiN sample. In particular, TiNSn5 showed *ca.* 22% of brookite (space group: *Pbca*; orthorhombic structure) and smaller crystallites, whereas the higher Sn content promotes the rutile phase (space group: $P4_2/mnm$; tetragonal structure), which is the only phase clearly appreciable. These phenomena can be explained on the grounds of the structural similarity of rutile TiO_2 and SnO_2-cassiterite (space group: $P4_2/mnm$; tetragonal structure), which can favour the growth of rutile at low temperatures (< 500–600 °C). Interestingly, XRPD analyses show no well-defined peaks related to SnO_2 segregated phases.

Zn-promoted samples show a marked decrease in crystallinity, which is already clear from the XRPD pattern of TiNZn5 (Fig. 1). This phenomenon can be rationalized considering the sharp difference among the crystalline habits of TiO_2 polymorphs and ZnO wurtzite (the most likely ZnO polymorph to form in the adopted synthetic conditions, space group: $P6_3mc$; hexagonal structure), which might inhibit the TiO_2 crystal growth in the presence of Zn species. As in the case of Sn-modified samples, no well-defined peaks related to segregated phases (ZnO polymorphs) are appreciable from XRPD patterns, even at the highest Zn content (Fig. 1).

The structural modification in terms of anatase cell distortion is highlighted by the shift of the anatase (101) diffraction peak towards lower 2θ values for both N- and metal-modified samples with respect to the pristine Ti material (Fig. S1). A shift of 0.05° was recorded in the case of N- and N,Zn-modified samples, with respect to the pristine material. A distortion of the anatase cell was previously reported by Lo Presti and co-authors [23] in the case of N-doped samples. A more marked shift (0.1°) was recorded in the case of TNSn5. It is worth noting that the TiNSn20 sample shows a phase transition to rutile.

These results suggest a higher affinity of Sn species for the titania lattice with respect to the Zn species, due to either the same oxidation