Catalysis Today 209 (2013) 54–59

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

Influence of the chemical synthesis on the physicochemical properties of N-TiO_2 nanoparticles

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ARTICLE INFO

Article history:
Received 29 June 2012
Received in revised form 30 October 2012
Accepted 14 December 2012
Available online 6 March 2013

Keywords:
MC-LR
N-TiO_2
Photocatalysis
Visible light

ABSTRACT

Nitrogen doped TiO_2 materials were successfully prepared following three different preparation routes (sol–gel, hydrothermal and pyrolysis) and characterized by various spectroscopic techniques. All samples absorbed radiation in the visible range and were active in the photocatalytic degradation of cyanotoxin microcystin-LR under visible light and in acidic conditions. The different preparation routes led to the formation of various impurities into the solids. In the case of hydrothermal and sol–gel samples, these impurities were weakly bound at the surface whereas the materials prepared by pyrolysis, the impurities showed a relevant stability and could not be removed even at high temperature. These species can affect the photocatalytic performance in different ways depending on their bulk or surface nature. On the basis of the photocatalytic data illustrated in this paper, the presence of such species at the surface was not detrimental for the photocatalytic activity of nitrogen doped TiO_2 but actually contributed to a higher interaction with the target cyanotoxin; leading to a higher photocatalytic activity than that observed for samples prepared via the classic sol–gel method.

1. Introduction

TiO_2 finds many applications in water and air purification using light (photocatalysis), however, it is well known that pure TiO_2 displays its unique photochemical and photophysical properties only under UV irradiation due to the high band gap value (3.2 eV for anatase polymorph) compatible only with the energy of UV photons. For this reason, many efforts have been spent in the past to extend the photocatalytic performances of TiO_2 to the visible region in order to exploit more efficiently solar light in all types of photocatalytic reactions [1].

Different strategies have been followed until now to reach this target such as doping with transition metal ions or surface sensitization with organic and organometallic dyes. More recently, doping TiO_2 with p-block (N, F, C, S) elements and in particular with nitrogen, has attracted the attention of the photocatalytic community as the introduction of such elements in the crystalline network produces materials capable of absorbing photons corresponding to visible radiation [2–5].

In previous work, research in our groups has shown that N doped TiO_2, known since 2001 [6] to have some photocatalytic activity under visible light (VLA), when prepared by wet chemistry methods contains photoactive centres based on interstitial N atoms bound to lattice oxygen ions which are excited by photons of about 440 nm. These centres (labelled as $N_iO^{\bullet}$) are paramagnetic and were identified via Electron Paramagnetic Resonance (EPR) spectroscopy [7–9].

A significant number of papers on N doped titania have appeared in the past few years, mainly focused either on new photocatalytic results or on different approaches to unravel the nature of the bulk photoactive centres present in this system while a systematic study on the role of several other factors of vital importance for the photocatalytic process are still lacking. Among these factors we recall: (i) the preparation procedure of the photocatalyst, (ii) the nature of the impurities present in the material and (iii) the state of the surface after preparation. In the present contribution we report results concerning different N doped TiO_2 materials prepared by three distinct wet chemistry methods (sol–gel synthesis, hydrothermal synthesis and pyrolysis) in order to investigate the relationships between the preparation procedure, the physicochemical properties of the materials and their photocatalytic properties.

All materials were first characterized to ensure the presence of N photoactive centres and, secondly, to identify the presence of other centres formed during preparation in order to understand their role on the promotion or inhibition of the photochemical phenomena. It is reported in the literature, in fact, that a high level of doping does not necessarily correspond to a high photocatalytic performance [10,11]. The dopant element, in fact, usually leads to

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http://dx.doi.org/10.1016/j.cattod.2012.12.020

active species for photocatalysis under visible light but, at the same time, it can form species having a detrimental effect on the material photoactivity [12]. The ratio between these two forms of nitrogen containing species can be affected by the followed preparation route.

The evaluation of these materials was performed in engineered water processes for the photocatalytic degradation of microcystin-LR (MC-LR); a widely found cyanotoxin in various water sources worldwide. Cyanotoxins are secondary metabolites with diverse chemical structure that are released from different genera of harmful cyanobacteria during bloom events. They are highly soluble in water, chemically stable and pose high toxicity (as hepatotoxicity, cytotoxicity or neurotoxicity) which represents a potential health risk to humans and the environment. MC-LR has been selected as target contaminant since it has been intensively investigated due to its continuous presence in higher concentrations than the provisional guideline for potable water proposed by the World Health Organization (1 μg/L). Previous work indicates that MC-LR can be subject to photocatalytic degradation with conventional and non-metal doped TiO_2 under UV and visible light [13–17].

2. Materials and methods

Three different methods for the preparation of N-doped TiO_2 were employed in this work. The first one was the classic sol gel synthesis (hereafter SG), via hydrolysis of titanium isopropoxide and NH_4F as nitrogen source, as described elsewhere [18]. The second method was the hydrothermal synthesis (HT) based on the treatment of a TiO_2 xerogel (typically 0.8 g) in the presence of 25 ml NH_3 for 5 days at 430 K in a 125 ml hydrothermal reactor. The third material was synthesized via pyrolysis (PY) heating a mixture of Ti-isopropoxide, ethanol, urea and a 0.5 M HCl solution (molar ratio 2:70:7:1 respectively) for 30 min in a furnace preheated at 573 K. All materials after synthesis underwent a final calcination in air at 773 K for 1 h.

The structural characterisation was performed by X-ray diffraction (XRD) using a Philips 1830 diffractometer (K_α(Co) source) and a X'Peret High-Score software for data handling. Surface area was measured by a surface area analyzer (ASAP 2020, Micromeritics – USA). UV–vis diffuse reflectance (DR UV–vis) spectra were recorded by a Varian Cary 5/UV-Vis-N.I.R. spectrometer using a Cary win-UV scan software to follow the visible absorption enhancement due to nitrogen doping. Table 1 summarizes the main properties (see S.I. also) of the prepared N-TiO_2 materials.

Electron Paramagnetic Resonance (EPR) spectra were run on an X-band CW-EPR Bruker EMX spectrometer operating at 100 kHz field modulation.

FTIR (Fourier Transform Infra-Red) spectra were obtained by a Brucker IFS 66 spectrophotometer equipped with an MCT cryogenic detector. The samples were inspected in the form of pellet in a FTIR cell connected to a conventional high-vacuum apparatus (residual pressure < 10^{-3} Pa) which allowed a heat treatment of the samples.

An on-line Thermal Gravimetric Analysis coupled with Fourier Transform Infra-Red instrument (TGA–FTIR) from Perkin-Elmer (Waltham, MA, USA) was used to simultaneously analyze the weight loss of the powders and the nature of the molecules released by the samples upon heating.

For the TGA analysis the ultra-microbalance Pyris 1 from Perkin-Elmer (sensitivity 0.1 μg) was used. The materials were heated under O_2 flow (30 $cm^3\,min^{-1}$) at a heating rate of 25 K min^{-1} in the 298–1173 K range. A relatively large amount of sample (c.a. 20 mg) was heated in each run to optimize the amount of gases released. FTIR analysis of the evolved gas was carried out by a Spectrum 100 (Perkin-Elmer) spectrometer in the 600–4000 cm^{-1}.The photocatalytic degradation of MC-LR was carried out in a batch system. The experiments were performed by adding a suspension of the nanoparticles (0.5 g/L), previously sonicated (2510R-DH, Bransonic), to an acidic solution (pH 3.0 ± 0.1) containing 600 ± 20 μg/L of MC-LR (Calbiochem). The photocatalytic reactor, a borosilicate glass Petri dish, was continuously mixed and irradiated under visible light (λ > 420 nm) with two 15 W fluorescent lamps equipped with a UV block filter (UV 420, Opticology). An average light intensity of $7.5 \times 10^{-5}\,W\,cm^{-2}$ was measured with a broadband radiometer (Newport Corporation). The quantification of the samples, previously filtered (L815, Whatman) and taken at specific interval times, was performed by liquid chromatography (LC, Agilent Series 1100). Details of the analytical method can be found elsewhere [19].

Table 1
summarizes the main properties (see S.I. also) of the prepared N-TiO_2 materials.

Sample	Dopant	Composition wt% (anatase)	Composition wt% (rutile)	Surface area (m^2/g)
HT	N	100	0	75
PY	N	90	10	48
SG	N + F	100	0	50

Main properties of the three types of N-TiO_2 materials (dopants, phase compositions and surface areas).

3. Results and discussion

3.1. EPR characterization

N-TiO_2 was characterized by the presence of paramagnetic species whose EPR spectrum has been widely discussed in previous work [4–6]. The main paramagnetic species (indicated as $N_iO^\bullet$) was present in all samples investigated (Fig. 1) and can be described in terms of interstitial nitrogen into the TiO_2 lattice. This species is the photoactive centre as proved on the basis of irradiation experiments showing that its EPR spectral intensity varies when irradiating the sample with suitable radiation [8,20].

Other nitrogen containing paramagnetic species observed in the materials here analyzed are NO (nitric oxide, present in the spectra of Fig. 1B and C) and NO_2 (nitrogen dioxide, traces in Fig. 1C) which are essentially by-products formed during the final calcination which do not influence the electronic structure of the solid.

Molecular $NO^\bullet$ and NO_2 are segregated in closed pores (or microvoids) within the crystals. Their EPR spectrum is not observable in the gaseous state but becomes visible at low temperature when the molecule is weakly adsorbed and polarized on a cationic

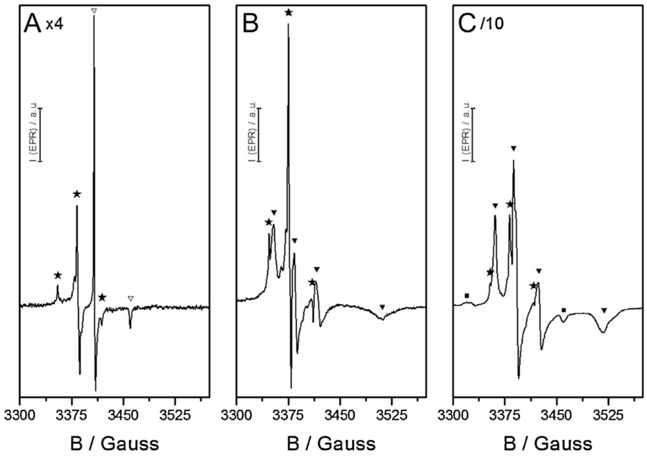

Fig. 1. EPR spectra of differently prepared N-TiO_2. (A) SG sample. (B) PY sample. (C) HT sample. Star indicates $N_iO^\bullet$ species; black triangle indicates $NO^\bullet$ species; white triangle indicates Ti^{3+} species; square indicates NO_2 species.