



Critical influence of surface nitrogen species on the activity of N-doped TiO₂ thin-films during photodegradation of stearic acid under UV light irradiation



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ABSTRACT

Atmospheric-pressure chemical vapour deposition (APCVD) was used to produce a series of nitrogen-doped titania (N-TiO₂) thin-films using *tert*-butylamine as the nitrogen source. The films were deposited as the anatase phase on glass and quartz substrates and characterised using X-ray diffraction, optical and vibrational spectroscopy and electron microscopy. The nature and location of the nitrogen species present on the surface and bulk of the films was studied by X-ray photoelectron spectroscopy. Thorough comparison amongst films with similar structural and morphological features allowed the role of nitrogen species to be evaluated during photo-oxidation of a model organic pollutant (stearic acid). Sequential photocatalytic experiments revealed a drastic decrease in the UV activity of the films which were correlated with changes involving surface nitrogen groups. The existence of concomitant nitrogen species with similar binding energies (*ca.* 400 eV) but different chemical nature is proposed, as well as the direct participation of at least one of these species in the oxidation reaction. A similar mechanism for the visible light activity of N-TiO₂ materials is also suggested.

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1. Introduction

The strategy of doping titania (TiO₂) using non-metal impurities in order to extend the photocatalytic efficiency of the semiconductor to include the visible range is one of the key challenges of photocatalysis. The prolific work reported by Asahi et al. [1] in which nitrogen doping was identified as a promising approach for an effective bandgap narrowing of TiO₂ has spawned active discussion and controversy in the last decade [2–6]. For the most part, the discussion around nitrogen-doped TiO₂ materials (henceforth N-TiO₂) has been focused on their visible light activity and its origins. Many authors have attributed the visible light activity as being due to localised N-2p midgap energy states in the band structure of TiO₂ upon substitution of O²⁻ by N³⁻ (substitutional N_s) species in the TiO₂ lattice [7]. Using X-ray photoelectron spectroscopy (XPS), the presence of N_s species in N-TiO₂ materials is widely assigned to binding energy peaks at *ca.* 397 eV in the N 1s environment. Some authors have suggested that the visible light activity is only indirectly related to the incorporation of substitutional nitrogen N_s in

the structure, but rather due to an optimum number of oxygen vacancies (V_{OS}) inherently formed in the doping process [4,7].

The confusion around the photocatalytic efficiency of N-TiO₂ materials has possibly occurred by the often questionable test methods used to assess visible light activity. For example, the photo-oxidation or photo-reduction of dye molecules under irradiation conditions can involve the direct participation of the dye in the reaction (dye-sensitised processes). However, many authors have claimed visible light activity during photodegradation of organic pollutants [1,8–10]. In the latter case, the main hurdle is in the design or setup of the experiment itself, the use of appropriate cut-off filters (even in the case of monochromated light that may include secondary bands at half-wavelength in the UV range), the control of any potential thermal degradation of the target organic pollutant, etc. In addition, many studies have involved photocatalysts with very different physical properties (crystallinity, morphology, surface area, etc.), undetermined ratios of TiO₂ polymorphs, etc., which hinder an appropriate comparison between the efficiencies of doped and undoped compounds. Likewise, the actual incorporation (*doping*) of nitrogen in the material can often be disputed, particularly in works involving the post-treatment of TiO₂ compounds.

In most cases, visible light activity in photocatalysts has been observed to the detriment of UV light activity and a possible

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existence of two opposing mechanisms has been suggested [4]. The presence of N species in interstitial positions (interstitial N_i) in the TiO_2 lattice has been proposed in the case of enhanced UV light activity of some N- TiO_2 materials [11]. It is generally accepted that the interstitial nitrogen atoms occupy positions as neutral species (N^0) in the bulk of the TiO_2 lattice. Nevertheless, the nature of these N_i species, with binding energy at ca. 400 eV, remains unclear and other species, such as chemisorbed molecular nitrogen ($\gamma-N_2$) and NH_x groups have been suggested [4,12].

In the current work, further insight is provided into the origin of the enhanced UV activity, as well as the nature and role of N_i species in N- TiO_2 materials. N- TiO_2 thin-films were synthesised using atmospheric-pressure chemical vapour deposition (APCVD) and their photoactivity was evaluated during photodegradation of octadecanoic (stearic) acid, a model organic pollutant. The deactivation of these materials upon UV cleaning and after sequential stearic acid tests and its correlation with chemical changes involving surface N species suggest the direct participation of surface N groups in the enhanced UV activity observed for some N- TiO_2 materials.

2. Experimental

2.1. Chemical vapour deposition apparatus and film synthesis

All components of the CVD apparatus including gas lines and CVD reactor were kept at high temperature. The precursors were heated independently in stainless steel bubblers and the vapour generated was carried into stainless steel mixing chambers at 250 °C using pre-heated nitrogen gas (BOC). Plain nitrogen (N_2) flow carried the mixture of gas precursors through a triple baffle manifold into the reactor. The CVD reactor consisted of a 320 mm-long graphite block contained in a quartz tube, which was heated by three Whatman heater cartridges. Pt–Rh thermocouples were used to control the temperature of the individual components of the CVD rig.

All chemicals used in this work were purchased from Sigma–Aldrich. Titanium chloride ($TiCl_4$, 99.9%), ethyl acetate ($C_4H_8O_2$, 99%) and tert-butylamine ($C_4H_{11}N$, 99.5%) were used as titanium, oxygen and nitrogen sources, respectively. In a typical deposition, the bubbler temperatures of Ti, O and N sources were constant at 340, 310 and 278 K, respectively. The latter temperature was set using an ice bath. The corresponding mass flow rates of Ti and O sources were also constant, 6.7×10^{-3} and 3.1×10^{-3} g min^{-1} , respectively. The flow rates of the N source are indicated in Table 1. The films were deposited at 773 K, either on quartz slides (25 mm \times 25 mm \times 4 mm, Multi-Lab) or float glass substrates (89 mm \times 225 mm \times 4 mm, supplied from Pilkington NSG Group). The glass substrates were fabricated with a silica (SiO_2) barrier layer to prevent ion diffusion into the film. The substrates

were thoroughly cleaned using acetone (C_3H_6O , 99%), isopropanol (C_3H_8O , 99.9%) and distilled water and dried in air prior to use.

2.2. Analytical methods

X-ray diffraction (XRD) studies were performed using a Bruker-Axs D8 (GADDS) diffractometer equipped with a monochromated ($K\alpha_1$ and $K\alpha_2$) Cu X-ray source and a 2D area X-ray detector with a resolution of 0.01°. The films were analysed with a glancing incident angle (θ) of 5°. The diffraction patterns obtained were compared with database standards. Raman spectroscopy was carried out using a Renishaw 1000 spectrometer equipped with a 514 nm laser. The Raman system was calibrated using a silicon reference. Absorption spectroscopy was performed using a double beam, double monochromated Perkin Elmer Lambda 950 UV/vis/NIR Spectrophotometer. The absorption spectra were recorded directly on the films as deposited on quartz slides, clamped against an integrating sphere in perpendicular position to the beam path. A Labsphere reflectance standard was used as reference in the UV/vis measurements. The thickness of the films was typically estimated using the Swanepoel method [13] using reflectance spectra in the range 300–2500 nm, recorded on a Helios double beam instrument standardised relative to a silicon mirror. The estimated thickness of selected films was confirmed using side-view scanning electron microscopy (SEM). SEM analysis was carried out using secondary electron image on a JEOL 6301 field-emission instrument (5 kV). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific™ K-alpha™ spectrometer, with monochromated Al $K\alpha$ radiation, a dual beam charge compensation system and constant pass energy of 50 eV. Survey scans were collected in the energy range of 0–1200 eV. High-resolution peaks were used for the principal peaks Ti (2p), O (1s), N (1s), C (1s) and Si (2p). The peaks were modelled using sensitivity factors to calculate the film composition. The area underneath these bands is an indication of the concentration of element within the region of analysis (spot size 400 μm).

2.3. Photocatalytic test and irradiation conditions

The photodegradation of stearic acid was monitored via Fourier transform infrared (FTIR) spectroscopy in the range 2700–3000 cm^{-1} , using a Perkin Elmer RX-I instrument. A thin film of stearic acid was dip-coated onto the photocatalytic films from a 0.05 M stearic acid solution in chloroform. The IR spectra were collected in absorbance mode and the integrated areas of typical C–H bands of the acid at 2958, 2923 and 2853 cm^{-1} monitored upon illumination (Fig. 1). These bands give an estimation of the number of molecules of stearic acid degraded using a conversion factor reported in the literature ($1 cm^{-1} \equiv 9.7 \times 10^{15}$ mol) [14]. The photoactivity rates were estimated from linear regression of the initial 30–40% degradation steps (zero-order kinetics). These rates may be

Table 1

Film description and experimental details for the deposition of undoped (Ti1) and N-doped TiO_2 (NTi-) films. The temperature and mass flow conditions were constant for metal ($TiCl_4$) and oxygen ($C_4H_8O_2$) precursors: 340 and 310 K, and 6.7×10^{-3} and 3.1×10^{-3} g min^{-1} , respectively.

Sample	Mass flow N source $\times 10^{-3}$ (g min^{-1})	Growth rate (nm min^{-1})	R_0 ($cm^{-1} h^{-1}$)	FQE $\times 10^{-4}$ (mol photon $^{-1}$)
Ti1	–	355	0.078	0.92
NTi1	1.262	390	0.195	2.30
NTi2	0.643	360	0.105	1.24
NTi3	0.598	410	0.094	1.11
NTi4	0.561	335	0.083	0.98
NTi4/UV	–	–	0.029	0.34
NTi4/H ₂ O	–	–	0.047	0.56
NTi5	1.338	330	0.218	2.77
NTi5'	–	–	0.103	1.30
NTi5''	–	–	0.085	1.08

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