Critical influence of surface nitrogen species on the activity of N-doped TiO\textsubscript{2} thin-films during photodegradation of stearic acid under UV light irradiation

Raul Quesada-Cabrera*, Carlos Sotelo-Vazquez, Jawwad A. Darr, Ivan P. Parkin**

University College London, Department of Chemistry, Christopher-Ingold Laboratories, 20 Gordon Street, London WC1H 0AJ, United Kingdom

Abstract

Atmospheric-pressure chemical vapour deposition (APCVD) was used to produce a series of nitrogen-doped titania (N-TiO\textsubscript{2}) 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 coconitant 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-TiO\textsubscript{2} materials is also suggested.

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1. Introduction

The strategy of doping titania (TiO\textsubscript{2}) 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 TiO\textsubscript{2} has spawned active discussion and controversy in the last decade [2–6]. For the most part, the discussion around nitrogen-doped TiO\textsubscript{2} materials (henceforth N-TiO\textsubscript{2}) has been focused on their visible light activity and its origin. Many authors have attributed the visible light activity as being due to localised N–2p midgap energy states in the band structure of TiO\textsubscript{2} upon substitution of O\textsuperscript{2–} by N\textsuperscript{3–} (substitutional N\textsubscript{s}) species in the TiO\textsubscript{2} lattice [7]. Using X-ray photoelectron spectroscopy (XPS), the presence of N\textsubscript{s} species in N-TiO\textsubscript{2} 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\textsubscript{s} in the structure, but rather due to an optimum number of oxygen vacancies (V\textsubscript{O\textsubscript{2–}}) inherently formed in the doping process [4,7].

The confusion around the photocatalytic efficiency of N-TiO\textsubscript{2} 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 TiO\textsubscript{2} 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 TiO\textsubscript{2} compounds.

In most cases, visible light activity in photocatalysts has been observed to the detriment of UV light activity and a possible...
existence of two opposing mechanisms has been suggested [4]. The presence of N species in interstitial positions (interstitial N\textsubscript{I}) in the TiO\textsubscript{2} lattice has been proposed in the case of enhanced UV light activity of some N-TiO\textsubscript{2} materials [11]. It is generally accepted that the interstitial nitrogen atoms occupy positions as neutral species (N\textsuperscript{0}) in the bulk of the TiO\textsubscript{2} lattice. Nevertheless, the nature of these N\textsubscript{I} species, with binding energy at ca. 400 eV, remains unclear and other species, such as chemisorbed molecular nitrogen (\gamma-N\textsubscript{2}) and NH\textsubscript{3} 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\textsubscript{I} species in N-TiO\textsubscript{2} materials. N-TiO\textsubscript{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\textsubscript{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\textsubscript{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 barrier layer to prevent ion diffusion into the film. The substrates were thoroughly cleaned using acetone (C\textsubscript{2}H\textsubscript{4}O, 99%), isopropanol (C\textsubscript{3}H\textsubscript{6}O\textsubscript{2}, 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 (Ka\textsubscript{1} and Ka\textsubscript{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 JSM 6701 field-emission instrument (5 kV).

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific™ K-alpha™ spectrometer, with monochromated Al K\textalpha 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) 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\textsuperscript{-1}, using a Perkin Elmer RX-1 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\textsuperscript{-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\textsuperscript{-1} = 9.7 × 10\textsuperscript{15} mol) [14]. The photodegradation rates were estimated from linear regression of the initial 30–40% degradation steps (zero-order kinetics). These rates may be

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass flow N\textsubscript{source} × 10\textsuperscript{-3} (g min\textsuperscript{-1})</th>
<th>Growth rate (nm min\textsuperscript{-1})</th>
<th>R\textsubscript{0} (cm\textsuperscript{-1} h\textsuperscript{-1})</th>
<th>FQE × 10\textsuperscript{-4} (mol photon\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1</td>
<td>355</td>
<td>0.078</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>NTi1</td>
<td>1.262</td>
<td>390</td>
<td>0.195</td>
<td>2.30</td>
</tr>
<tr>
<td>NTi2</td>
<td>0.643</td>
<td>360</td>
<td>0.105</td>
<td>1.24</td>
</tr>
<tr>
<td>NTi3</td>
<td>0.598</td>
<td>410</td>
<td>0.094</td>
<td>1.11</td>
</tr>
<tr>
<td>NTi4</td>
<td>0.561</td>
<td>335</td>
<td>0.083</td>
<td>0.98</td>
</tr>
<tr>
<td>NTi4/UV</td>
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<td>–</td>
<td>0.029</td>
<td>0.34</td>
</tr>
<tr>
<td>NTi4/H\textsubscript{2}O</td>
<td>–</td>
<td>–</td>
<td>0.047</td>
<td>0.56</td>
</tr>
<tr>
<td>NTi5</td>
<td>1.338</td>
<td>330</td>
<td>0.218</td>
<td>2.77</td>
</tr>
<tr>
<td>NTi5'</td>
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<td>–</td>
<td>0.103</td>
<td>1.30</td>
</tr>
<tr>
<td>NTi5''</td>
<td>–</td>
<td>–</td>
<td>0.085</td>
<td>1.08</td>
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</table>
Fig. 1. (a) Typical IR spectra collected during the photodegradation of stearic acid on a N-TiO2 film over 25 h. (b) Integrated areas of stearic acid bands estimated during UVA illumination of undoped (full circles) and N-doped (full diamonds) TiO2 films. The areas obtained from the acid on plain glass are included for reference (empty circles). The corresponding photocatalytic rates were calculated from linear regression of the initial 30–40% degradation steps (grey lines).

given as formal quantum efficiency (FQE) values, which are defined as the number of acid molecules degraded per incident photon. The overall degradation reaction is:

\[
\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H} + 26\text{O}_2 + 2\text{N}_2\text{O}_2\text{TiO}_2(\text{hv} \geq E_{bg}) \rightarrow 18\text{CO}_2 + 18\text{H}_2\text{O} \tag{1}
\]

A blacklight-bulb (BLB) UVA lamp (Vilber-Lourmat), 2 × 8 W, was used in the photocatalytic tests. The irradiance of the UV lamp (1.2 mW cm\(^{-2}\)) was measured using a UVX meter (UVP). Further visible light tests were carried out using a solar simulator (AM1.5), 75 W Xe lamp (PTI QuantaMaster\textsuperscript{TM}400), with a cut-off 420 nm filter (VMI). The irradiation area of the samples was 0.78 cm\(^2\). The as-deposited films were UV cleaned under wet-air conditions during 24 h and kept in the dark for at least 24 h previous to any photocatalytic activity test.

3. Results and discussion

3.1. Film characterisation

A range of N-TiO\(_2\) thin-films were deposited by APVCD of titanium tetrachloride (TiCl\(_4\)), ethyl acetate (C\(_4\)H\(_8\)O\(_2\)) and tert-butylamine (C\(_4\)H\(_{11}\)N) on glass and quartz substrates at 500 °C. The as-deposited films were in the thickness range within 350–420 nm (Table 1). In general, it was observed that the introduction of low N levels (<1 at.%, as determined by XPS) had little or no impact on the physical properties of the doped films compared to undoped samples. These N-TiO\(_2\) films were pure anatase and no traces of rutile, titanium nitride or any other nitrogen-containing structures were detected by XRD and Raman spectroscopy (Fig. 2).

Fig. 2. (a) Typical X-ray diffraction patterns (\(\lambda = 1.5406\) Å) and (b) Raman spectra of undoped (black line) and N-doped (grey line) TiO\(_2\) thin-films deposited using tert-butylamine as nitrogen source (<1 at.% N). These are representative films considered for the photocatalytic assessment. (c) Absorption spectra of typical undoped (black line) and N-doped (grey line) TiO\(_2\) films (<0.5 at.% N) used in the photocatalytic testing. The spectra of N-TiO\(_2\) films containing relatively high N total concentrations (>1 at.% N) have been included for comparison (dashed lines). (d) Typical surface and bulk XPS data from the N 1s environment of an as-deposited N-TiO\(_2\) film. The bulk data represents an average of the spectra collected during Argon sputtering of the film. General assignments of XPS peaks have been included.
reported in the literature [7,15,16]. In addition, traces of additional phases, which likely corresponded to oxynitride compounds, were detected in the latter films using Raman spectroscopy. Thus, only N-TiO2 films which contained low nitrogen levels (<1 at.% N) were considered for the photocatalytic assessment in this work, to allow a fair comparison with similar undoped TiO2 reference samples.

The undoped TiO2 films were colourless and translucent, showing an absorption onset at ca. 380 nm and maximum absorbance at 330 nm (Fig. 2(c)), whereas the N-TiO2 films used in the photocatalytic testing were typically yellow and their corresponding absorption edge was red-shifted with respect to that of the undoped films. Some N-TiO2 films with relatively high content of nitrogen (>1 at.% N) showed additional absorption bands in the range of 400–450 nm, as shown in Fig. 2(c). All of these absorption features are consistent with previous reports [4,7,17–19].

The nature and concentration of N species incorporated in the N-TiO2 films were studied by XPS and their influence on the photoactivity of these materials is discussed in the following section (vide infra). As stated above, nitrogen can be incorporated into the TiO2 structure in oxygen lattice sites (as N3−, substitutional Ns) or in interstitial positions (as N0, interstitial Ni), which are commonly assigned to binding energies of ca. 397 and 400 eV, respectively, by XPS analysis [1,4,6,7]. All the as-deposited N-TiO2 films showed a single binding-energy peak at 400.6 eV (Ni) on the surface and both environments (Ns and Ns), i.e. different ratios of the peaks at 397.6 and 400.6 eV, in the bulk of the films (Fig. 2(d)). It should be noted that the peak at 400.6 eV on the surface of N-TiO2 materials has also been widely assigned to chemisorbed nitrogen (γ-N2), as indicated in the figure. Nevertheless, the latter peak was not observed in the XPS analysis of undoped TiO2 films, despite the fact that nitrogen (N2) is used as a carrier gas during the APCVD synthesis. Hence, we do not consider chemisorbed nitrogen as being the progenitor of the 400 eV XPS peak.

### 3.2. Influence of the nitrogen environment on the photoactivity of N-TiO2 films

The overall impact of nitrogen doping on the photoactivity of N-TiO2 films was investigated via photodegradation of stearic acid, as described in the experimental section. Comparable undoped (Ti1) and doped TiO2 films (NTi1, NTi2 and NTi3), which showed similar XRD patterns (Fig. 4(a)), were investigated in the initial photocatalytic tests carried out under UVA illumination (BLB lamp, 1.2 mW cm−2). Bulk average XPS analysis of these films showed very similar Ni levels (397.6 eV) but different concentrations of surface and bulk Ns species (400.6 eV) (Fig. 4(b)). The corresponding UV activities of these films, given as formal quantum efficiencies (units, mol photon−1), and relative content of the different N species are

![Fig. 3. Scanning electron microscopy (SEM) images (25,000×) of representative undoped (a) and N-doped (b) TiO2 films as deposited using tert-butylamine as nitrogen source.
](image1)

![Fig. 4. (a) X-ray diffraction patterns (λ = 1.5406 Å) of selected N-TiO2 films (NTi1, NTi2 and NTi3) and as-deposited undoped TiO2 film (Ti1) used as reference. (b) Corresponding XPS spectra of surface (left) and bulk average (right) species in the N 1s environment (assignments included). (c) Respective formal quantum efficiencies. The relative levels (%) of surface (empty circles), interstitial (full diamonds) and substitutional (full triangles) nitrogen are indicated for comparison.
](image2)
indicated in Fig. 4(c). A general increase in activity, compared to the undoped TiO$_2$ sample (Ti1), was initially observed for the N-TiO$_2$ films which contained high levels of N$_i$ species (NTi1). In contrast, the activity of N-TiO$_2$ films with very low N$_i$ levels (NTi3) was comparable to that of the undoped Ti1 film, despite the relatively high content of substitutional N$_s$ species in the former film. Thus, the enhanced UV activity of N-TiO$_2$ films was attributed to the influence of N$_i$ species alone, in agreement with previous observations by the authors[11]. Indeed, the trend of activities observed for samples NTi1, NTi2 and NTi3 followed the relative concentrations of N$_i$ species estimated from XPS data, as inferred from Fig. 4(c). Further insight into the role of these species in the apparent enhancement of the UV activity of N-TiO$_2$ films will be discussed in the following section (vide infra).

Stearic acid tests were also carried out under visible light irradiation (75 W Xe lamp, AM1.5 and cut-off UV filter) over 3 days, however, no visible activity was detected for any of our N-TiO$_2$ films beyond instrumental error. Many authors have reported visible light activity during photodegradation of organic pollutants using N-TiO$_2$ materials and correlation with N species with binding energies of ca. 397 eV (N$_s$) has been suggested [1,8–10]. These species were only found in the bulk of our films together with interstitial N species and it is unclear whether the presence of the latter would have a detrimental effect on the potential visible light activity of the films.

### 3.3. Photostability of N-TiO$_2$ films

Sequential photoactivity tests were carried out under UVA irradiation in order to investigate the photostability of the N-TiO$_2$ films. After each test, the sample was washed in pure chloroform under stirring conditions to eliminate any trace of stearic acid and a new layer of acid was deposited for subsequent testing. Surprisingly, it was found that the activity rates progressively dropped (Fig. 5) until reaching a minimum value, which corresponded to those expected for comparable undoped TiO$_2$ films. XPS analysis of the surface of the N-TiO$_2$ film (NTi4) after sequential tests showed a concomitant decrease in area of the peak at 400.6 eV (N$_i$) and a weak new peak at 407.6 eV. The latter has been assigned to the binding energy of NO$_3^-$ ($N_5^+$) species [20].

Insight into the nature of the binding-energy peak at 400.6 eV on the surface of N-TiO$_2$ films and its role in the apparent photoactivity of these materials were further investigated upon UV cleaning of the films. UVA (or UVC) irradiation of synthesised photocatalysts is common practise to clean the surface of the materials of residual organic contaminants. However, we found that UVA cleaning of the as-deposited N-TiO$_2$ films under high humidity (wet-air) conditions caused important changes on the surface N species, as detected by XPS. Fig. 6(a) illustrates the effect of UVA illumination (1.2 mW cm$^{-2}$) on a typical N-TiO$_2$ film (NTi5). It can be observed that, after irradiation for 48 h, the initial surface peak at 400.6 eV (N$_i$) decreased to approximately half of the initial area (NTi5/UV) and a new XPS peak at 407.6 eV appeared. This observation suggests that the partial photo-oxidation of the N species with binding energy of 400.6 eV resulted in the formation of NO$_3^-$ groups on the surface of the film. These chemical changes had a detrimental effect on the photocatalytic performance of the film (Fig. 6(b)), as...
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4. Conclusions

N-TiO2 thin-films were synthesised using atmospheric-pressure chemical vapour deposition. The films were deposited as single-phase anatase and contained different ratios of interstitial (N\textsubscript{i}) and substitutional (N\textsubscript{s}) nitrogen species, as evidenced by XPS depth profiling, with binding energies at 400.6 and 397.6 eV, respectively. The surface N species identified showed binding energies at ca. 400 eV, typically assigned to interstitial N\textsubscript{i} and chemisorbed molecular nitrogen (γ-N\textsubscript{2}). However, the latter was not observed in the undoped TiO\textsubscript{2} samples, despite the use of nitrogen as carrier gas in the deposition of the films.

The as-deposited N-TiO\textsubscript{2} films showed enhanced UV activities compared to those of similar undoped TiO\textsubscript{2} samples, which were correlated with levels of interstitial N species at 400 eV. Nevertheless, a decrease in UV-photoactivity was observed after sequential stearic acid tests and also after UV cleaning of the doped films. These observations were related to a concomitant decrease in the XPS peak at 400 eV. Once this peak reached a minimum, the activity of the N-TiO\textsubscript{2} film was similar to that of a comparable undoped sample.

It was concluded that the surface XPS peak at ca. 400 eV was due to the presence of concomitant N species, in agreement with some literature reports. Direct participation of active N groups (likely NH\textsubscript{4} species) in the photodegradation reaction mechanism was proposed, likely involving highly oxidising N–O radicals. These active species would form nitrate (NO\textsubscript{3}\textsuperscript{−}) groups in the absence of an organic pollutant, as observed in this work. At the same time, inactive interstitial nitrogen N\textsubscript{i} groups are assigned for the peak at 400 eV, which remains after the degradation reaction.

No visible light activity was observed for any of the films investigated in this work. However, the deactivation of N-TiO\textsubscript{2} materials reported by some authors suggests that surface N species could be responsible for the apparent visible light activity claimed in some cases in the literature.

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