Single-step synthesis of doped TiO$_2$ stratified thin-films by atmospheric-pressure chemical vapour deposition†

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

Locally doped TiO$_2$ thin-films were engineered by pulsed precursor delivery using atmospheric-pressure chemical vapour deposition. To our knowledge, this is the first example of stratified films deposited in this manner. The optical, structural and morphological properties of the films were investigated using absorption spectroscopy, X-ray diffraction and electron microscopy techniques. Nitrogen-doped TiO$_2$ stratified thin-films were produced as proof that the new technique would work and that the nature and location of nitrogen species within the films could be studied by X-ray photoelectron spectroscopy. The photocatalytic performance of the films was investigated using the photodegradation of a model organic pollutant (stearic acid). The impact of a stratified configuration and the influence of the type of nitrogen species on enhanced photocatalytic activity are discussed.

1. Introduction

Titania (TiO$_2$) thin-films have been used in a wide range of photocatalysis applications, including water and air-cleaning technologies, water-splitting, self-cleaning materials and degradation of cancer cells and viruses. This is due to its high efficiency in the UV range, chemical inertness, mechanical robustness and relatively low cost. In the last decade, strenuous efforts have been devoted to broaden the photoresponse of TiO$_2$ into the visible range for solar photocatalysis applications. Some of these approaches include the design of TiO$_2$-based composite materials, the modification of TiO$_2$ using dye sensitizers and the incorporation of metal or non-metal ions into the TiO$_2$ structure. An interesting strategy, particularly adopted in recent years, is the selective incorporation of dopants (local doping) into semiconductor photocatalyst materials. Local doping typically allows control over structural defects and contributes to a better understanding of the physicochemical properties of the doped materials and their effect on photocactivity. Regardless of the potential benefits of ion-doping in terms of band-structure and electronic-properties, the indiscriminate addition of dopants into TiO$_2$ host materials, may have a drastic impact on physical properties (crystallinity, morphology, etc.), thus affecting their photocatalytic performance. This has certainly been the case in the synthesis of doped semiconductor films via chemical vapour deposition (CVD).

A local doping approach in the synthesis of films using CVD may not only minimise any structural impairment in the material but also produce systems with similar properties to those synthesised via atomic layer deposition (ALD). ALD is widely used to produce nanostructured thin-films with controlled thickness and crystallinity facilitating the engineering of stratified films containing buffer layers for a facile and rapid separation of charge carriers for solar cell applications. This is the case of nanostructured TiO$_2$ shells and ZnO–TiO$_2$ films, where recombination of photogenerated carriers on ZnO are quenched by ultrathin TiO$_2$ layers, improving the efficiency of solar cell devices.

The selective incorporation of dopants into TiO$_2$ films can be easily achieved by pulsed precursor delivery using CVD. This method involves the introduction of the dopant precursor only during intermittent periods of total deposition time. In the current work, anatase stratified nitrogen-doped TiO$_2$ films were synthesised in this manner. This is, to the best of our knowledge, the first example of stratified doped photocatalytic thin-films synthesised by CVD. It is different to ALD because the process does not rely on monolayer coverage and subsequent chemical reaction. In this work we found that despite the high nitrogen content of the locally doped regions in the stratified films, their overall crystallinity was apparently unaffected in the doping process, as evidenced by X-ray diffraction. This allowed a fair comparison among similar undoped, non-stratified and stratified samples and correlation between the nature and concentration of the dopant and their influence on photocatalytic activities during degradation of a model organic pollutant. The enhanced activity of stratified N-TiO$_2$ films will be discussed. Nitrogen was chosen here as a model dopant, since N-doped TiO$_2$ materials have been extensively studied.

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investigated, however, the local doping approach can be easily applied to any dopant or mixtures of co-dopants and it represents a promising new strategy in the design and development of a new generation of photocatalysts and other layered systems.

2. Experimental description

All chemicals were purchased from Sigma-Aldrich. Titanium chloride (TiCl₄, 99.9%), ethyl acetate (C₄H₈O₂, 99%) and tert-butylamine (C₄H₁₁N, 99.5%) were used as titanium, oxygen and nitrogen sources, respectively.

The CVD reactor

All the components of the CVD apparatus were kept at high temperature (200 °C). The precursors were heated independently in stainless steel bubblers in order to generate enough vapour pressure to be carried into the reactor. Pre-heated nitrogen (supplied by BOC) was used as carrier gas. The vapour pressure of the mixture of gas precursors through a triple baffle manifold producing a wide laminar flow into the reactor. The CVD reactor was a 320 mm-long heated graphite block with three inserted Whatman heater cartridges. The carbon block was contained in a quartz tube and the temperature controlled using Pt–Rh thermocouples.

In a typical deposition, titanium chloride (TiCl₄) and ethyl acetate (C₄H₈O₂) were used as titanium and oxygen sources, respectively. The experimental conditions set for titanium and oxygen precursors were constant in the deposition of all undoped and doped TiO₂ films, with bubblers temperatures of 340 and 310 K and mass flow rates of 6.7 × 10⁻³ and 3.1 × 10⁻³ g min⁻¹, respectively. The film growth of the resulting undoped TiO₂ films was ca. 350 nm min⁻¹ (Table 1). All films were deposited at 500 °C on float glass substrates (89 × 225 × 4 mm) supplied by the Pilkington NSG Group, which is pre-coated with a SiO₂ barrier layer by the company in order to prevent ion diffusion into the film. The glass substrates were thoroughly cleaned using acetone (99%), isopropanol (99.9%) and distilled water and dried in air prior to use. Details of the particular experimental conditions for the synthesis of the films investigated in this work are given below.

**Analytical methods**

X-ray diffraction (XRD) analysis was performed using a Bruker-Axs D8 (GADDS) diffractometer. The instrument operates with a Cu X-ray source, monochromated (Kα₁ and Kα₂) and a 2D area X-ray detector with a resolution of 0.01°. Films were analysed with a glancing incident angle (θ) of 5°. The diffraction patterns obtained were compared with database standards. UV/Vis spectroscopy was performed using a double monochromated Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer in the 300–1000 nm range. Reflection spectra was recorded for different positions in the range 300–2500 nm on a Helios double beam instrument standardised relative to a silicon mirror, which allowed the thickness of the films to be determined via the Swanepoel method. The latter measurements were confirmed for selected samples using side-view scanning electron microscopy (SEM). The SEM studies were carried out using a JEOL 6301 (5 kV) and a JEOL JSM-6700F field emission instruments and the Oxford software INCA. X-Ray photoelectron spectroscopy (XPS) was performed using a Thermo 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 range of 0–1200 eV. High-resolution peaks were used for the principal peaks of 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).

**Photocatalytic test**

The photocatalytic performance of the films synthesised in this work was evaluated during photodegradation of octadecanoic acid (stearic) acid (95%, Sigma-Aldrich). A Perkin Elmer RX-I Fourier transform infrared (FTIR) spectrometer was used to monitor the degradation of stearic acid under UVA illumination. Black light blue (BLB) lamps (Vilber-Lourmat, 2 × 8 W, 365 nm, 1.2 mW cm⁻²) were used for the photocatalytic tests. In addition, regular indoor-light (fluorescent) lamps (GE lighting 2D fluorescent GR10q-835 white, 28 W) were used to test the activity of the films in the visible range.

**Table 1** Film description and experimental details for the deposition of undoped and N-doped TiO₂ thin-films. The temperature and mass flow conditions were constant for metal (TiCl₄) and oxygen (C₄H₈O₂) precursors: 340 and 310 K and 6.7 × 10⁻³ and 3.1 × 10⁻³ g min⁻¹, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample description</th>
<th>N mass flow (×10⁻³) (g min⁻¹)</th>
<th>Deposition time (s)</th>
<th>Film growth (nm min⁻¹)</th>
<th>Total N content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1</td>
<td>Undoped</td>
<td>—</td>
<td>60</td>
<td>305</td>
<td>—</td>
</tr>
<tr>
<td>Ti2</td>
<td>Undoped</td>
<td>—</td>
<td>120</td>
<td>355</td>
<td>—</td>
</tr>
<tr>
<td>N1</td>
<td>Non-stratified doped</td>
<td>5.9</td>
<td>60</td>
<td>265</td>
<td>2.0</td>
</tr>
<tr>
<td>N2</td>
<td>Non-stratified doped</td>
<td>1.0</td>
<td>120</td>
<td>340</td>
<td>0.25</td>
</tr>
<tr>
<td>SL</td>
<td>Single-layer doped</td>
<td>1.3</td>
<td>60/30⁰</td>
<td>390</td>
<td>0.60</td>
</tr>
<tr>
<td>ML</td>
<td>Multi-layer doped</td>
<td>1.3</td>
<td>120/25⁰</td>
<td>330</td>
<td>0.65</td>
</tr>
</tbody>
</table>

a Fraction of total time for nitrogen precursor delivery.
3. Results and discussion

Synthesis of stratified nitrogen-doped films

The deposition of nitrogen-doped TiO$_2$ films (N-TiO$_2$) was carried out controlling the high vapour pressure of the nitrogen precursor (C$_4$H$_{11}$N) by cooling down the bubbler to 275 K using a dry ice bath. The film growth of N-TiO$_2$ films typically ranged between 300–340 nm min$^{-1}$, depending on the nitrogen precursor flow rates as determined from side-on SEM. A pulsed delivery of the nitrogen precursor was set so that highly doped regions were intercalated with undoped regions in the deposition of stratified films. Three-dimensional XPS images of the N 1s environment of doped N-TiO$_2$ films are shown in Fig. 1. The yellow areas in the images indicate highly doped regions in the films. In the case of non-stratified films, the nitrogen precursor was allowed to flow during the entire deposition time (Fig. 1(a)). A single-layer stratified film (SL) was synthesised by allowing the introduction of nitrogen during half the time of total deposition (30 s) (Fig. 1(b)) and the same process was followed in 5 s intervals for the production of a multi-layer stratified N-TiO$_2$ film (Fig. 1(c)). The corresponding flow rates and deposition conditions are listed in Table 1.

The undoped TiO$_2$ films deposited were colourless and transparent (Fig. 2, inset), showing interference fringes due to thickness gradients across the samples. In contrast, the N-TiO$_2$ films were yellow (Fig. 2, inset) and their corresponding absorption spectra showed a red-shift of the absorption edge compared to undoped TiO$_2$ films (Fig. 2). This shift was not significant in the case of single-layer N-TiO$_2$ films compared to undoped samples, both types showing threshold wavelengths in the range of 375–385 nm (3.2–3.3 eV), nevertheless, highly doped samples showed important shifts toward the visible range and two optical absorption thresholds were apparent near 460 and 570 nm (2.7 and 2.2 eV), respectively. It is worth noting that no difference was found between comparable non-stratified and stratified N-TiO$_2$ films in terms of their absorption properties and also that these estimations ignore the scattering component in the spectra. Similar changes have been reported in the incorporation of nitrogen into TiO$_2$ materials in the literature,

and the potential activity of N-TiO$_2$ materials is a matter of historic controversy.

All undoped and N-doped films investigated in this work had similar surface morphologies and cross-sectional growth (Fig. 3). SEM analysis showed large star-shaped aggregated particles apparently unaffected by nitrogen doping. However, the incorporation of high concentrations of nitrogen had an impact on the crystallinity of the N-TiO$_2$ films, as evidenced by XRD analysis (Fig. 4(a)). The broadening and decrease of the anatase diffraction peaks was clearly observed when comparing undoped and doped films of similar thickness. This is in agreement with similar observations reported in the literature. In contrast, XRD studies of stratified films containing selected regions of comparable nitrogen concentration showed intense, sharp peaks (Fig. 4(c)), suggesting that their overall crystallinity was largely unaffected by the high doping levels.

The corresponding XPS patterns averaged from a similar thickness range of these films (ca. 50 nm) are shown in Fig. 4(b and d). The concentration of nitrogen was estimated from integration of the area underneath each XPS curve in the N 1s environment (397–400 eV). These spectra include one highly doped layer in the case of the stratified ML film. It can be clearly observed that the nitrogen levels within selective regions of

![Fig. 1 X-ray photoemission three-dimensional view of the N 1s environment from depth analysis of selected N-TiO$_2$ thin-films: (a) non-stratified, (b) single-layer stratified and (c) multi-layer stratified doped films. The yellow areas indicate regions of high nitrogen concentration. The main peak in the N 1s environment has been assigned to substitutional nitrogen species (397 eV).](image)

![Fig. 2 UV/Vis spectra of typical undoped (a) and N-TiO$_2$ thin-films: (b) single-layer (SL), (c) non-stratified (N2) and (d) multi-layer (ML) films using tert-butylamine as nitrogen source. The inset shows photographs of typical undoped TiO$_2$ and N-TiO$_2$ films synthesised by CVD.](image)

![Fig. 3 Scanning electron microscopy (SEM) images of typical (a) undoped and (b) stratified N-TiO$_2$ films. (c) Side-view SEM of the multi-layer ML N-TiO$_2$ film.](image)
both films were comparable, 0.70 and 0.50, for N1 (non-strati-
fied) and ML (stratified) samples, respectively.

The strategy of pulsed precursor delivery offered an oppor-
tunity to study the effect of a stratified arrangement of highly
doped regions in otherwise similar N-TiO$_2$ films in terms of
physical properties.

**Photoactivity of stratified vs. non-stratified films**

The photocatalytic activity of these films was evaluated upon
degradation of a model organic pollutant, octadecanoic (stearic)
acid, under UVA irradiation (1.2 mW cm$^{-2}$). The overall degra-
dation reaction is given by eqn (1).

$$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H} + 2\text{O}_2 \rightarrow \text{TiO}_2 / h\nu \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$  \[1\]$$

The films were coated with a thin layer of stearic acid using
an in house built dip-coater from a 0.05 M stearic acid solution
in chloroform. A typical photoactivity test monitoring the pho-
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tone in the samples, suggesting that there is likely a direct
correlation of the nature and concentration of N species in the
films and their photoactivities.

The influence of N species on the photocatalytic activity of
N-TiO₂ materials is a matter of great controversy in the litera-
ture. Nitrogen may be incorporated in substitutional (β-N,
oxide lattice site) and interstitial (γ-N) environments into the
TiO₂ structure, with corresponding binding energies of 397 and
399–400 eV. The specific influence of β- and γ-N species on
the photoactivity of N-TiO₂ compounds has been extensively
discussed, however, no agreement has been reached in
this regard. In our case, the photocatalytic behaviour of our
samples in the UV range (Fig. 5(c)) did not follow a particular
trend for either β- or γ-N species. The content of substitutional
nitrogen (β-N, 397 eV) in the multi-layer ML sample was very
high compared to those in single-layer SL and non-strati
N₂ films (Fig. 6(b)), which could explain the peak activity of the
former. However, the β-N concentration in both SL and N₂
samples is very similar, in contrast to their corresponding
activities. On the other hand, the levels of interstitial nitrogen
species (γ-N, 400 eV) were comparable in both ML and N₂
samples and only slightly higher in the single-layer SL film
(Fig. 6(b)).

Some authors have also reported the role of nitrogen
adsorbed species in the efficiency of N-TiO₂ photocatalysts and
it is not clear if a synergistic interaction among bulk and
adsorbed species is required for the best performance of these
materials. In our work, XPS analysis of the N 1s environment
on the surface showed a peak at 400 eV, which has been
commonly assigned to surface adsorbed nitrogen species (γ-N,
NO₃, NH₃). The amount and nature of these surface adsorbed
nitrogen species were also comparable among our films and no
trace of other nitrogen-containing species (N²⁺, NO₃⁻, etc.) was
detected.

In addition, other authors have highlighted the potential role of oxygen vacancies (VOS), particularly focusing
on their visible activity, which are inherently generated in the
incorporation of N³⁻ anions into the TiO₂ structure (intrinsic
defects) and also formed under the reductive conditions
typically used during nitrogen doping. According to these
authors, the photocatalytic activity of N-TiO₂ materials in the visible
range correlates with an optimal number of VOS, above which
VOS would act as carrier recombination centres. Further
photocatalytic studies were carried out in the visible range
using regular indoor fluorescent lamps, however, no activity
was observed beyond instrumental error for any of the films
used in the discussion of this work.

The implication for a direct correlation between photo-
activity and total concentration of nitrogen in the films is
important, admitting that the stratified N-rich regions could act
as buffer layers that favour the generation of charge carriers.
In this case, a valid explanation for the unexpectedly high
activity of the stratified films may be proposed in terms of
mobility of photogenerated charge carriers. The stratified film is
then engineered to contain a combination of N-doped layers,
for an increased production of charge carriers, and undoped
regions of high mobility, band-like conduction behaviour, for
an optimum photocatalytic performance (Fig. 7). In contrast,
high nitrogen densities present across the entire non-stratified
film could act as carrier recombination centres, having a
detrimental impact to their photoactivity.

4. Conclusions

A new strategy to synthesise stratified doped TiO₂ films using
atmospheric-pressure chemical vapour deposition (APCVD)
has been presented. This is to our knowledge the first
example of APCVD to be used in pulsed precursor delivery.
High concentrations of nitrogen were selectively incorpo-
rated during the deposition of TiO₂ anatase films with minor
detriment of their overall crystallinity, as suggested by XRD
studies. The photocatalytic activity of the resulting stratified
films was investigated during degradation of stearic acid. The
activity of these films was dramatically enhanced compared
to similar non-stratified and undoped films. A possible
explanation for this enhancement has been proposed in terms of
the combined effects of high charge carrier photogeneration
and high mobility, low carrier recombination
within highly doped and undoped regions of the stratified
films.

Examples of advanced catalyst design such as the one pre-
presented in this paper urge to a revision of the widely-studied
photocatalytic systems for an optimum combination of their
physicochemical properties. The selective addition of appro-
riate amounts of a particular dopant (or mixture of co-dopants)
adds yet another variable to the complexity of these systems.
The simple strategy employed here for the incorporation of
controlled concentrations of nitrogen into TiO₂ films can be
used to produce materials with multiple layers using a limited
range of dopants. In this sense, the approach is similar to that
used in atomic layer deposition and it allows configuration of
multi-layer stratified films for the best advantage of carrier
generation and mobility.

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Notes and references