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Ultra-violet light activated photocatalysis in thin films of the titanium oxynitride, $Ti_{3-\delta}O_4N$

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ABSTRACT

A film of the recently reported material $Ti_{3-\delta}O_4N$ has been shown to be more photocatalytically active than a comparable film of TiO_2. The photocatalytic ability was determined using the stearic acid degradation test with 254 nm UV light. Both films were made using atmospheric pressure chemical vapour deposition (APCVD) at 630 °C from titanium (IV) chloride and ethyl acetate, with the oxynitride additionally using ammonia as a nitrogen source. The films were characterised by XRD and spectroscopic methods. The Raman pattern of $Ti_{3-\delta}O_4N$ is also reported here for the first time.

1. Introduction

There is increasing interest in materials that exhibit semiconductor photocatalysis for the purposes of self-cleaning materials [1], dye-sensitised photovoltatics and in the production of H_2 fuel *via* the photo-activated splitting of water [2,3]. Photocatalysis is the process in which an ultra band-gap photon is absorbed by a semiconductor particle to produce an electron–hole pair, which can then migrate to the surface of the crystallite and take part in redox reactions to photomineralise absorbed molecules, *via* the generation of radical species [4]. In principle any semiconducting material can be used for photocatalysis, however in many materials extensive recombination and unsuitable valance and conduction band energies prevent any appreciable photocatalytic activity being observed. This, amongst other factors such as cost and durability, mean that only a limited number of materials have been identified as practical photocatalytic materials. These include CdS [5] and $SrTiO_3$ [6] but particularly TiO_2, the anatase phase of which is most widely used in applications due to a combination of high activity, low cost and ease of synthesis in a variety of forms suitable for applications, including nanoparticles and thin films [7–10]. It should be noted, however, that some authors report that mixed anatase and rutile systems actually show an enhanced activity over either pure sample [11].

$Ti_{3-\delta}O_4N$ is a recently discovered titanium oxynitirde with the pseudo-brookite structure, related to one of the magneli phases of titanate, Ti_3O_5 [12]. It crystallises in the *CmCm* space group with a cell volume of approximately 364 Å^3, varying slightly depending upon the exact titanium deficiency. The formation of $Ti_{3-\delta}O_4N$ as a thin film has been published previously [13], using atmospheric pressure chemical vapour deposition (APCVD) from titanium (IV) chloride, ammonia and ethyl acetate. Spectroscopic investigation found that the material absorbed in the visible region of the electromagnetic spectrum, indicating the possibility of visible light photocatalysis.

In the work presented here we describe the observation of photocatalysis in $Ti_{3-\delta}O_4N$ thin films, again synthesized using APCVD, and report the results of tests comparing the rate of photocatalysis to TiO_2 films, similarly made using APCVD. These results present the possibility of $Ti_{3-\delta}O_4N$ as a photocatalyst competitive to TiO_2 in terms of reaction rate, and a material that can be readily made using existing coating technologies, with a similar cost and durability to TiO_2 films.

2. Results

A film of $Ti_{3-\delta}O_4N$ was synthesized using APCVD from titanium (IV) chloride, ethyl acetate and ammonia. A film of TiO_2 was also synthesized, for comparative purposes, using identical conditions but without the nitrogen source of ammonia. Both films formed were adherent (they passed the scotch tape test) and appeared by eye to be pin-hole free. The TiO_2 film was colourless, and the $Ti_{3-\delta}O_4N$ film green in colour. Thin films made *via* static CVD coaters will often have a gradient or some degree of variation across the substrate, due to temperature gradients and reactant depletion. So

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to average out these potential differences two square sections of 25 × 25 mm^2 were cut from each of the films, one 60 mm from the leading edge and one 130 mm; these sample coupons were then used as test sections to characterise the films and determine their photocatalytic ability.

2.1. X-ray diffraction

The diffraction patterns recorded on the TiO_2 film sections contained peaks that could be matched to the positions of database patterns of the rutile and anatase polymorphs. Fig. 1a shows the diffraction pattern of the front section of the titania film. However the relative intensities of the peaks for each phase did not match predicted patterns, due to the presence of preferred orientation, a common occurrence in films made by CVD [14]. The presence of this preferred orientation effectively removes most of the information contained within the peak intensities, and as such it is impossible to determine accurately the ratio of the anatase:rutile phases present in each film section. This ratio is an important consideration as the photocatalytic effect is widely reported as being higher in the anatase polymorph. For this reason the composition was estimated by comparing the areas of the most intense peak for each of the two phases, the 1 1 0 peak of rutile, and the 1 0 1 peak of anatase. In the section taken from 60 mm in from the leading edge, this ratio was 15:85, rutile:anatase, and in the section from 130 mm along the ratio was 55:45. (Values to nearest 5%).

The diffraction patterns recorded on the sections of $Ti_{3-\delta}O_4N$ gave peaks that could be indexed in the *CmCm* space group by Le bail refinement, with lattice parameters of $a = 3.803(1)$ Å, $b = 9.626(1)$ Å and $c = 9.879(1)$ Å for the 60 mm section; for the 130 mm section lattice parameters of $a = 3.811(1)$ Å, $b = 9.635(7)$ Å and $c = 9.885(1)$ Å were found; no additional un-indexed peaks were present in either pattern. These cell indices match well with previously reported values for $Ti_{3-\delta}O_4N$ of $a = 3.8040(1)$ Å, $b = 9.6486(1)$ Å and $c = 9.8688(1)$ Å [13]. Preferred orientation present in both section of the titanium oxynitride film prevented a full Rietveld refinement, however the Le Bail refinement was sufficient to identify the phase present in the films as $Ti_{3-\delta}O_4N$. Fig. 1b shows one of these patterns with indexing.

From the diffraction data we can also estimate, using the Scherrer equation, the size of the crystallites in the films. Crystallite size is one of the factors that determines the rate of photocatalysis in TiO_2, because it is believed that the particle boundaries act as recombination sties for electrons and positive holes – thus it is desirable to minimise to the surface to bulk ratio by having a large average crystallite size. This analysis found that the average crystallite sizes in the titania film were 29(2) nm and 30(1) nm for the 60 mm and 130 mm sections, while in the $Ti_{3-\delta}O_4N$ film the sections had average crystallite sizes of 27(5) nm and 29(5) nm for the 60 mm and 130 mm sections respectively. The values found from the analysis of our films show that all have a similar crystallite size, of just less than 30 nm in size. This similarity means that the crystallite size should not be factor controlling any differences seen in the photocatalytic activities of the films, and so the materials can be compared without concern that this particular aspect might affect the result.

2.2. Spectroscopy

Spectroscopic measurements were conducted in transmission from 300 nm to 2500 nm, on both sections of both films; these are shown in Fig. 2. The spectra of the TiO_2 film sections have the characteristic strong transmittance, >60%, in the visible and IR portion of the spectrum, dropping dramatically around 500 nm, as the band gap of the material is approached. In the transparent region oscillations in the transmittance are observed as a function of wavelength, these are the results of interference of internal reflections within the film. The positions of the maxima and minima can be used to determine the thickness of the film with the Swanepoel method [15], giving for the titanium film thicknesses of 538(9) nm

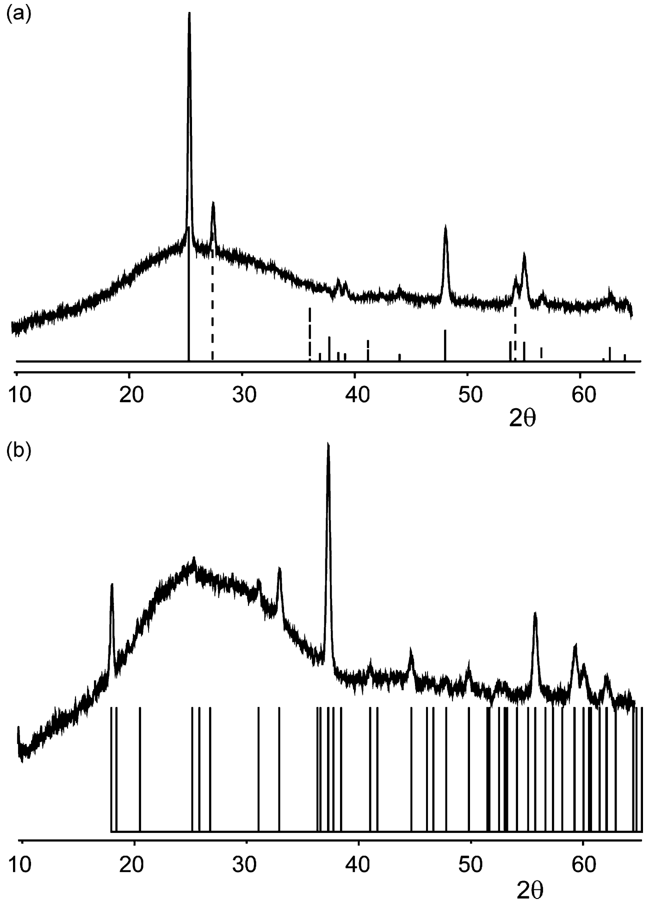

Fig. 1. X-ray diffraction patterns recorded on sections taken 60 mm from leading edge of film. (a) TiO_2 film. Solid line is database pattern of anatase, dotted line is pattern of rutile. (b) $Ti_{3-\delta}O_4N$. Stick pattern beneath shows indexing taken from a Le Bail fit.

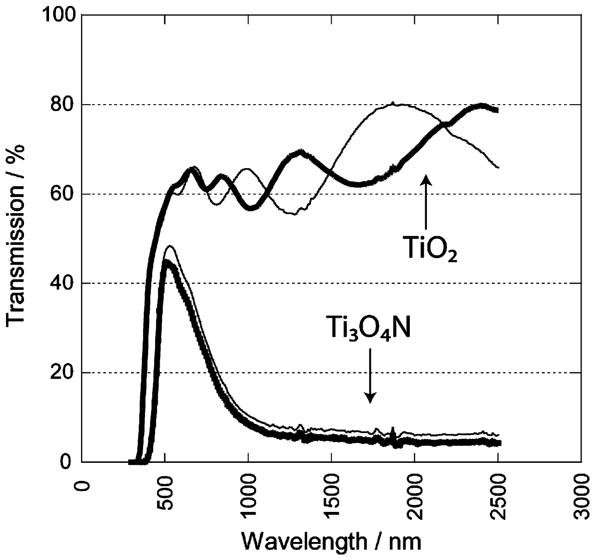

Fig. 2. Transmission spectra of the TiO_2 and $Ti_{3-\delta}O_4N$ films, recorded in the range 2500–300 nm, on sections taken 60 mm (thick line) and 130 mm (thin line) from the leading edge of each film.

Table 1
Thickness of the films at each of the test sections as determined by side on SEM.

Material	Ti_3O_4N	
Position (mm)	60	130
Thickness (nm)	440(50)	640(50)

and 411(8) nm for the sections 60 mm and 130 mm from the leading edge respectively.

The spectra of the oxynitirde film coupons are significantly different to those of the titania samples. The spectra show very weak transmittance throughout the infrared region, with increasing transmission in the visible (the maximum transmittance is at ~515 nm and consistent with the observed green colour of the film), and diminishing transmission as the bad gap is approached, below 500 nm. The very poor transmittance of the oxynitride film in the infrared portion of the spectrum suggests the possibility that the film can be used as an absorptive solar control coating. Such coatings are used to prevent the uptake of solar heat energy by preventing the radiation through windows in the region 800–1200 nm. The further investigation of this property is, however, beyond the scope of this work.

Analysis of the spectra of $Ti_{3-\delta}O_4N$ by the Tauc method gives a value for the band gap of 2.6(1) eV for the material. The method could not be applied to the TiO_2 film, because the band gap of the substrate glass is comparable to that of TiO_2. Instead this value may be compared to literature reports which give a band gap value of 3 eV for rutile and 3.2 eV for anatase.[16,17]

Raman spectroscopy was also carried out on each of the sections, using a green 532 nm laser source. The sections taken from the TiO_2 film give similar patterns, with all the observed peaks (638 cm^{-1}, 511 cm^{-1}, 395 cm^{-1}, 194 cm^{-1} and 144 cm^{-1}) being consistent with a combination of anatase and rutile, based on patterns that have been previously published [18]. This confirms the phase identification from the X-ray diffraction. Both sections of the titanium oxynitride film investigated for this give the same pattern, with no indication of any peaks that might correspond to a TiO_2 polymorph. The Raman pattern of $Ti_{3-\delta}O_4N$ contains four peaks (in cm^{-1}; 214s, 246s, 434vw, 646w) and is shown in Fig. 3.

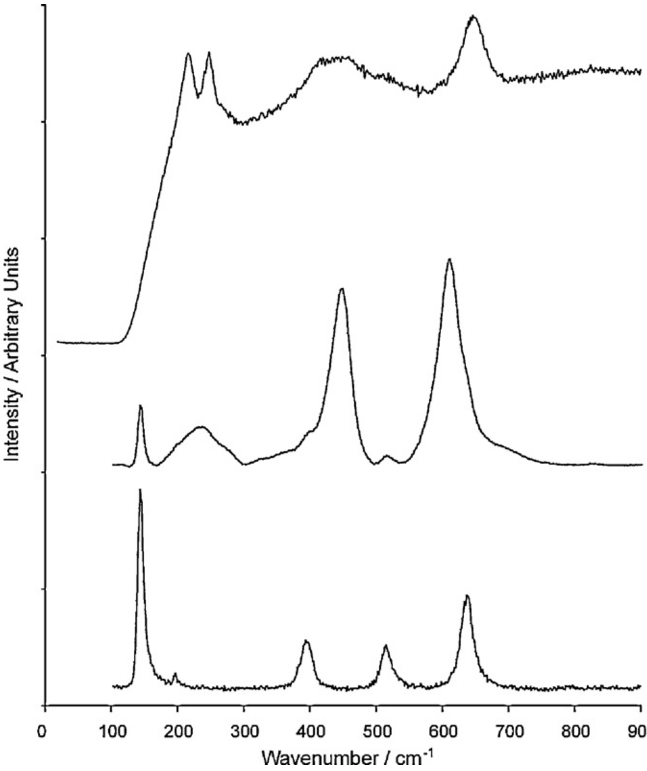

Fig. 3. Raman pattern of $Ti_{3-\delta}O_4N$ recorded using a green laser excitation source (top pattern). Below are given the Raman patterns of rutile (middle pattern) and anatase (bottom pattern) for comparative purposes.

2.3. Scanning electron microscopy

As the spectroscopic Swanepoel method could not be used to determine the thickness of the oxynitride film the less accurate side on SEM imaging was used to determine the thickness instead. Additionally top down SEM was used for both films to investigate film morphology. The values determined for the thickness of the two sections for each of the films is shown in Table 1. This found that all of the measured sections had thicknesses in the range of 400–650 nm. The values of 538(9) nm and 411(8) nm for the titania film are sufficiently similar to the thickness of the oxynitirde taken from SEM of 440(50) nm and 640(50) nm that the photocatalysis of the film sections can be reasonably compared without concern for over-riding thickness effects.

Top down SEM images of the same sections of the films were taken, and from these the morphology of the films could be observed. The images recorded of the TiO_2 film showed densely packed crystallites of approximately 300 nm diameter. The oxynitride film was composed of similarly densely packed plate like crystallites of approximately 200 nm diameter and 50 nm thickness. Fig. 4 shows examples of images taken from each material.

2.4. Stearic acid testing

Stearic acid testing is a widely used and convenient method for determining a relative rate for photocatalytic ability [10,19,20]. A solution of 0.01 M of stearic acid ($C_{17}H_{35}COOH$) in methanol was used to deposit a coating of stearic acid by evaporation onto the titanium oxide/oxynitride films. The coated films were then exposed to 254 nm light to photo-activate the films such that they would degrade the stearic acid. The amount of stearic acid

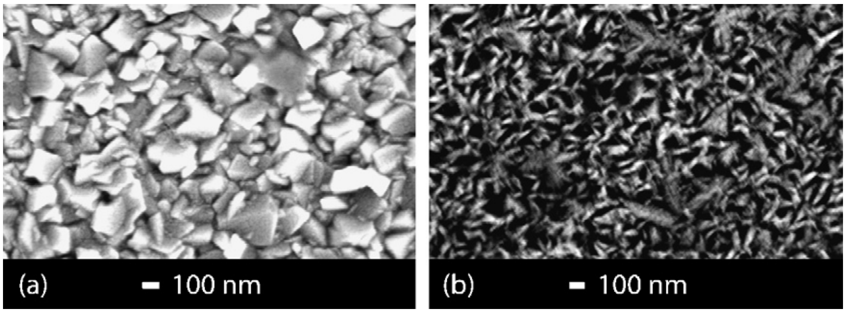

Fig. 4. Example top down SEM images, showing film morphology. (a) TiO_2 film, (b) $Ti_{3-\delta}O_4N$ film.

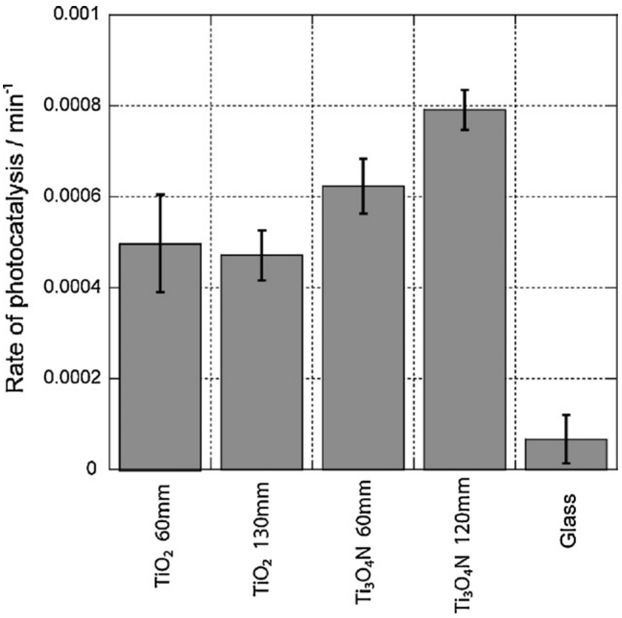

Fig. 5. 1st order rate constants for the destruction of stearic acid averaged over the three trials, conducted using 254 nm UV light.

deposited initially, and periodically during the degradation, was assessed by IR spectroscopy. The test was carried out on all four film sections simultaneously, and the trial carried out three times. Plain glass was used as a control in each of the experiments.

Using 254 nm UV light both the TiO_2 film sections, and the $Ti_{3-\delta}O_4N$ were found to be photo-active. Plots of the stearic acid concentration against time indicated that the degradation was occurring under 1st order kinetic conditions, as has been observed previously [21]. The 1st order rate constants for the degradation were determined from this data. This could be done for each of the films and the glass standards in all three trials. Fig. 5 shows a plot of these rate constants for each of the film sections averaged over the three trails.

Photocatalytic activity in TiO_2 using 254 nm light was of course expected; however, this is the first time that $Ti_{3-\delta}O_4N$ has been reported to be an active photocatalyst. The first order rate constants, shown in Fig. 5, are $6.2(5) \times 10^{-4}$ min^{-1} and $7.9(4) \times 10^{-4}$ min^{-1} in the $Ti_{3-\delta}O_4N$ film (60 mm and 130 mm section respectively) and of $5(1) \times 10^{-4}$ min^{-1} and $4.7(5) \times 10^{-4}$ min^{-1} for the TiO_2 film (60 mm and 130 mm section respectively). Both films showed significantly greater activity than the uncoated glass of $0.7(5) \times 10^{-4}$ min^{-1} where the degradation is due solely to UV absorption by the stearic acid. Significantly then, the $Ti_{3-\delta}O_4N$ is shown to have a greater photocatalytic rate than TiO_2 in these results.

Tests were also conducted using a 16 W fluorescent lamp visible light source, but these found that neither TiO_2 nor $Ti_{3-\delta}O_4N$ showed activity greater than the uncoated glass standard after 265 h of exposure. All samples exhibited a stearic acid decomposition rate of around 2×10^{-6} min^{-1}, but as this represents less than 2% decomposition over the 265 h exposure, and was also observed in the uncoated glass sample, it seems that such a rate is due evaporation and direct decomposition by the light source, rather than photocatalysis from the films. This is the expected result for TiO_2, and also shows that $Ti_{3-\delta}O_4N$ is not a visible light photocatalyst.

2.5. Contact angle

The contact angle for a 1 μl drop of water was measured on the film sections, after 24 h in the dark and after 24 h irradiation with 254 nm light. The results of these tests are given in Table 2.

Table 2
Contact angle of 1 μl drops of water on the surface of the films.

Material	TiO_2		Ti_3O_4N	
Position (mm)	60	130	60	130
24 h in dark	71°	85°	71°	39°
24 h under 254 nm	12°	9°	25°	12°

Both sections of the TiO_2 show a large drop in contact angle after irradiation from above 70° to around 10°, an effect known as super-hydrophilicity, often associated with photocatalytic materials and advantageous for self-cleaning properties, as it allows water to 'sheet' across the surface of the film, carrying surface contaminants with it [1]. In the $Ti_{3-\delta}O_4N$ samples this effect is also observed, the decrease in contact angles being around 50°, compared to a decrease of over 60° in TiO_2.

3. Discussion

The X-ray diffraction, Raman, spectroscopy and SEM measurements show that thin films of TiO_2 and Ti_3O_4N were successfully made on glass substrates with thickness in the range 320–660 nm. These were then tested for photocatalytic ability *via* the stearic acid test.

The visible light photocatalysis testing found no activity in either film sample, an expected result for TiO_2, but perhaps somewhat incongruous for the Ti_3O_4N film for which the Tauc analysis of the UV–vis spectra gave a band gap for the material of 2.6(1) eV, equivalent to visible light with a wavelength of 480 nm. One would expect such a band gap to be ideal for visible light photocatalysis, contrary to what is observed. The evidence of activity with 254 nm light suggests that the valance band and conduction band are suitably positioned in energy to allow photocatalysis, so an energy mismatch cannot be the cause of the inactivity. A possible explanation is that the energy levels associated with the absorption of visible photons that lead to the observed colour are different to the larger band gap levels that are capable of activating photocatalysis.

The UV activated photocatalysis test showed that the Ti_3O_4N film had the same order of activity as the similarly made TiO_2 film and indeed was slightly more active, with 1st order rate constants in the range of 4.7(5)–$7.9(4) \times 10^{-4}$ min^{-1}. As TiO_2 is used extensively in a wide range practical applications where photocatalytic ability is needed, the availability of a more active material, that may also be synthesized using inexpensive reagents, is an exciting possibility. However, although the results presented here show the Ti_3O_4N to be the more active *film*, it does not follow that Ti_3O_4N is the more active *material*.

Photocatalytic activity in thin films depends on a range of factors, including synthesis temperature, morphology, surface area, and thickness. Observed rates will also be proportional to the intensity of light used to activate the films. These effects can lead to observed rates with orders of magnitude difference for samples of the same material. For example the TiO_2 film shown here has a rate constant of $4.7–5 \times 10^{-4}$ min^{-1} for the destruction of stearic acid, while previous work has found rates as high as 84×10^{-4} min^{-1} for TiO_2 thin films [21]. An even greater variation was observed by Mills et al. when comparing thin films, with spin coated films from powder slurry where the higher surface area slurry film was found to have a rate of stearic acid destruction 18 times higher than a film produced by APCVD [8].

These comparisons indicate that the TiO_2 film used in these experiments has an activity much below the potential for titania. If the rates Ti_3O_4N observed in the experiments here are close to being the optimum of the material, then it is unlikely to be competitive as a potential replacement material. However the high values reported from the literature are the results of many years of study and several hundred publications annually into titania as a photocatalyst, as such one would not expect the first reported values for a new material to match those of a thoroughly investigated one. As such, although the results presented here show that $Ti_{3-\delta}O_4N$ is more active than TiO_2, it would be unwise to suggest it is the inherently more active material. instead what these results show is that photocatalytic activity is present in $Ti_{3-\delta}O_4N$ and that under certain synthetic conditions $Ti_{3-\delta}O_4N$ can be as active as TiO_2, and should be considered for applications as an alternative to TiO_2 in the future.

4. Conclusion

It has been shown that the recently elucidated material $Ti_{3-\delta}O_4N$ is a photocatalyst, and has an activity that compares favourably with the current 'market leader' TiO_2. Further work is need however, to determine it's efficacy for specific applications.

5. Experimental

Films of $Ti_{3-\delta}O_4N$ and TiO_2 were made for this study using atmospheric pressure chemical vapour deposition on glass substrates of dimensions $220 \times 85 \times 4\,mm^3$. The films were deposited in a cold walled reactor with the substrates placed in the reactor on a carbon block containing three Whatman heater cartridges. The substrates were made of standard commercial float glass, coated with a SiO_2 barrier layer to prevent the diffusion of ions from the glass into deposited films. Precursors were delivered to the reactor as vapours through two different entry points through a divided baffle manifold. All the details of this reactor have been published previously [13].

The $Ti_{3-\delta}O_4N$ film was made using titanium (IV) chloride, ethyl acetate and ammonia as precursors. The comparative TiO_2 film was made using identical conditions and precursors as the $Ti_{3-\delta}O_4N$ film, but without the addition of the nitrogen source, ammonia. Both the titanium (IV) chloride and ethyl acetate precursors were heated in brass bubblers through which nitrogen gas was passed to transport the vapours to the reactor. The $TiCl_4$ bubbler was heated to 65 °C and an N_2 transport gas flow of $2\,L\,min^{-1}$ was used – equivalent to $16\,mmol\,min^{-1}$. To transport the ethyl acetate a flow rate of $0.5\,L\,min^{-1}$ and bubbler temperature of 36 °C were used giving a flow rate of $5.4\,mmol\,min^{-1}$. Both these reagent vapour flows were combined in a mixing chamber with an additional plain line N_2 flow of $12\,L\,min^{-1}$ as a carrier gas. These conditions were used for the TiO_2 deposition and also for the $Ti_{3-\delta}O_4N$ deposition except that for the oxynitirde ammonia was introduced into the reactor through the second inlet at a flow rate of $0.26\,L\,min^{-1}$ using room temperature vapour pressure giving $11\,mmol\,min^{-1}$. A substrate temperature of 630 °C and reaction time of 30 s were used for both depositions. These experimental parameters for the formation of $Ti_{3-\delta}O_4N$ are identical to those previously reported for the synthesis of the material as a thin film [13], and those for the formation of TiO_2 were chosen to produce an oxide only film matched in thickness and crystallinity for comparative purposes; the use of similar reagents and conditions had also successfully shown the formation of a TiO_2 film previously [21,22].

The photocatalytic abilities of the four test film pieces and a glass blank standard were assessed with the widely used stearic acid degradation test. A film of stearic acid was deposited onto the samples by placing a 10 μl drop of 0.01 M solution of stearic acid in methanol onto the surface of the samples and allowing the solvent to evaporate. The thickness of the stearic acid layer was then assessed by IR spectroscopy in the region $2800–2960\,cm^{-1}$ where the organic C–H stretches appear in the spectrum. The samples were then exposed to 254 nm UV light supplied by two 8 W bulbs, and the thickness of the stearic acid layer periodically rechecked as the photo-activated surfaces degraded it, allowing the rate of photocatalysis to be determined for each analysed piece.

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