Efficient visible light-active N-doped TiO_2 photocatalysts by a reproducible and controllable synthetic route

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Received (in Cambridge, UK) 19th July 2006, Accepted 7th August 2006
First published as an Advance Article on the web 31st August 2006
DOI: 10.1039/b610316b

A reproducible and controllable method allows the synthesis of practical quantities of efficient, visible light active $TiO_2(N)$ photocatalysts in which the nitrogen content may be varied to achieve optimum performance.

Photocatalytic degradation of organic compounds on semiconductor surfaces is an important area of current research with respect to both fundamental understanding[1] and potential practical applications.[2] TiO_2, a promising, low-cost, robust photocatalyst is the most extensively investigated material in this field. However, its band gap (3.3 eV for anatase) is such that it can only be activated by *UV radiation* ($\lambda < 376$ nm). Given that such radiation corresponds to only $\sim 5\%$ of the incident solar flux at ground level, very large gains in efficiency of practical solar-powered photocatalytic systems are to be expected if they could be operated under visible light. Such materials would also be effective under artificial ambient light, for example, within buildings. As a result, intensive effort has been directed towards achieving this goal. An attractive strategy involves doping TiO_2 with low levels of nitrogen [hereafter $TiO_2(N)$], a process that red-shifts the absorption spectrum of titania.[2–8] However, it is important to note that the visible light photocatalytic activity of $TiO_2(N)$ is highly sensitive to the synthetic route used in its preparation: not infrequently, although such materials absorb visible light they are nonetheless totally inactive with respect to photocatalysis.[9] A possible explanation for this is that the photogeneration of electrons and holes is not in itself enough to impart photoactivity—in addition, the electron–hole recombination rate must also be low enough to permit a sufficient flux of these active species to reach the catalyst surface where they initiate reactions with adsorbed species. If practical applications are to be achieved, it is also necessary for the synthetic method to be (i) controllable, (ii) reproducible and (iii) low-cost. A variety of methods for N-doping of titania have been reported,[2–8] none of which meets all these conditions. Thus, although the hydrolysis of titanium precursors in the presence of a nitrogen source provides an inexpensive method of nitrogen doping,[5,8,10,11] the composition of the resulting $TiO_2(N)$ is difficult to control and cannot be systematically varied so as to establish the optimum composition for photoactivity. Thermal treatment of TiO_2 in an ammonia atmosphere results in significant reduction of Ti and substitutional doping with N.[12] Although the apparent N concentration can be varied by subsequent annealing, inhomogeneous nitrogen distribution within the sample impairs reproducibility and renders N concentration measurement by XPS difficult and possibly misleading.[2,12] Alternative routes such as ion implantation[2] can in principle permit some degree of control over the level of N-doping, albeit with unknown dopant depth distribution, but they are costly and unsuited to scale-up.

Here we describe a straightforward, low-cost and reproducible method for the synthesis of $TiO_2(N)$ by which the level of N-doping is readily controlled to yield effective visible light active photocatalysts.

A series of $TiO_2(N)$ catalyst precursors with nominal nitrogen doping levels in the range 0.2–1.0 wt% was prepared by a simple procedure involving the sequential reaction of H_2O with a small known excess of $TiCl_4$ in toluene (step 1) under dry, O_2-free argon, followed by stoichiometric reaction of the remaining $TiCl_4$ present with a standard solution of NH_3 in dioxane (step 2).

$$TiCl_4 + 2H_2O \xrightarrow{\text{step 1}} TiO_2 + 4HCl$$

$$3TiCl_4 + 4NH_3 \xrightarrow{\text{step 2}} \text{‘}Ti_3N_4\text{’} + 12HCl$$

It is unlikely that either step in this procedure will give rise to pure components. For example, in step 1 oxo-chlorides will also be formed [TiO_xCl_{4-2x}], the Ti–Cl groups of which will then react in the second step. Although we cannot fully exclude the possibility of some unreacted Ti–Cl or Ti–NH_n (n = 1–3) groups remaining in samples after reaction, few, if any, of these groups are likely to remain after final calcination. All reactions were performed under dry, O_2-free argon on a conventional glass vacuum line using a three-necked 2 dm^3 round-bottomed flask, equipped with an overhead magnetic stirrer and water-cooled reflux condenser. Greaseless fittings were used throughout in order to prevent contamination of samples. This included teflon sleeves on all joints, use of Youngs taps and a stirrer guide with chemically resistant o-rings. The stirrer guide was also equipped with a small (*ca.* 6 cm) water condenser in order to prevent chemical degradation of the rubber mountings during the reaction. In a typical reaction (here illustrated for a nominal 0.56 wt% sample), a solution of $TiCl_4$ (4.773 g) in toluene (500 mL) was reacted with H_2O (0.883 g) at room temperature. The mixture was then stirred (24 h). A solution of NH_3 in dioxane (0.5 mol dm^{-3}, 1.60 mL) was then added and stirred at room temperature (24 h), yielding a bright yellow suspension. This mixture was then brought to reflux (24 h), giving a light yellow suspension. The catalyst precursor was filtered off using a porosity 3 filter frit, washed with n-hexane then dried for 10 h under vacuum (10^{-2} bar) at room temperature.

In order to determine the optimum procedure for generating the final photocatalysts, samples of each precursor produced by the

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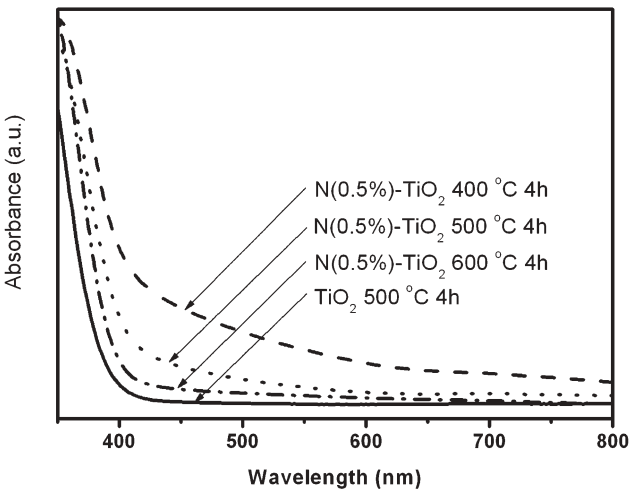

Fig. 1 UV-vis absorbance spectra of unmodified anatase and N-doped TiO_2 powders for different calcination temperatures.

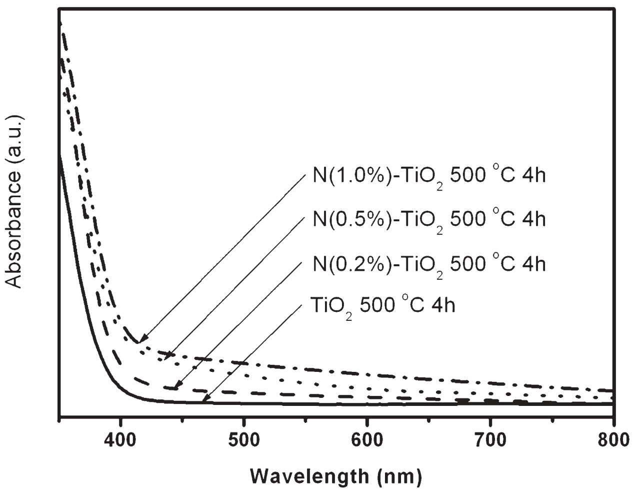

Fig. 2 UV-Vis absorbance spectra of unmodified anatase and N-doped TiO_2 powders for different concentrations of nitrogen.

above procedure were calcined in air at 400, 500, and 600 °C for 4 h and the resulting materials characterized by UV-vis reflectance spectroscopy. Fig. 1 illustrates results for the 0.5 wt.% N-doped material. Photocatalytic testing of these materials showed that (i) calcination at 400 °C resulted in a solid with pronounced absorption in the visible region but with no visible light photocatalytic activity (presumably the result of incomplete decomposition of the precursor phase), (ii) 500 °C calcination produced an effective (yellow) visible light active photocatalyst, and (iii) 600 °C resulted in an inactive (white) material (presumably the result of nitrogen depletion). A reference spectrum for calcined pure anatase is also shown in Fig. 1. Accordingly, a calcination temperature of 500 °C was used for all subsequent work in which the performance of a range of photocatalysts was evaluated under visible light illumination as a function of nitrogen content.

The BET surface areas, structure and mean crystallite sizes (XRD) for three different $TiO_2(N)$ catalysts are given in Table 1, along with reference data for pure anatase. It is apparent that all four materials were similar with respect to specific surface area but had somewhat different mean crystallite sizes, indicating some differences in particle size distribution.

Fig. 2 shows the corresponding UV-vis diffuse reflectance spectra. It is apparent that the optical absorption in the visible region (Fig. 2) increases with nitrogen content, as predicted theoretically by Lin *et. al.*[14] The shape of the absorption edge indicates that N-doping is primarily substitutional, with an insignificant concentration of oxygen vacancies.[14] XPS data confirmed successful incorporation of nitrogen into the TiO_2 and provided qualitative confirmation that the trend in measurable N concentration followed that to be expected from the synthetic procedure, but the poor signal : noise ratio precluded quantification. (It is well known that determination of small concentrations of N in TiO_2 is far from trivial.[13] Most analytical techniques do not work or are completely impractical in this case. Synchrotron photoemission provides a possible solution and such measurements are planned.)

Table 1 Properties of TiO_2 and $TiO_2(N)$ catalysts

Samples[a]	$S_{BET}/m^2\ g^{-1}$	Phase	Mean crystallite size/nm
TiO_2	97.96	Anatase	16.1
N(0.2)–TiO_2	99.94	Anatase	14
N(0.5)–TiO_2	95.26	Anatase	15
N(1)–TiO_2	94.95	Anatase	12.9

[a] All samples were calcined at 500 °C for 4 h.

In order to test the photoactivity of the $TiO_2(N)$ samples, the photocatalytic decomposition of methyl tertiary butyl ether (MTBE) was chosen: MTBE, a gasoline additive and potential carcinogen, is a pollutant that is of increasing concern in regard to public health. Photocatalytic measurements were carried out in a single-pass reactor under visible light irradiation using an ORIEL 1000 W Xe lamp (light intensity was 50 ± 5 mW cm^{-2} measured in 420–550 nm spectral range) with IR and visible filters selecting 420–770 nm spectral range. The catalyst (100 mg) was supported on a glass frit (I.D. 36 mm). MTBE vapour (68 ppm) and oxygen were supplied to the reactor at a total flow-rate of 44 mL min^{-1} (space velocity ~ 4 400 h^{-1}). The temperature of the illuminated samples was measured by an embedded thermocouple. A thin catalyst bed was used to minimise any gradients in temperature and light absorption. The steady state temperature of the catalysts did not vary substantially between samples (43–55 °C). Some variation is to be expected, given the different degrees of light absorption involved. *Control experiments in which the samples were heated in the absence of illumination showed that thermal effects were negligible so that the results refer to true visible light activity.* MTBE destruction and CO_2 production were monitored by gas chromatography (Shimadzu GC-14B equipped with FID and a capillary column, J&W Scientific Inc. 60 × 0.530 mm, dimethylpolysiloxane) and non-dispersive infrared spectrometry (SIEMENS ULTRAMAT-6) respectively.

The visible light photocatalytic activity as a function of nitrogen content is shown in Fig. 3. The results are given as % conversion of MTBE normalized with respect to specific surface area and measured by gas chromatography. Unmodified TiO_2 showed immeasurably low activity, as expected, given the bandgap of anatase. N-doping immediately induced visible light photocatalytic activity, with the 0.5 wt% nitrogen exhibiting the highest activity. It is important to note that this behaviour was reproducible with

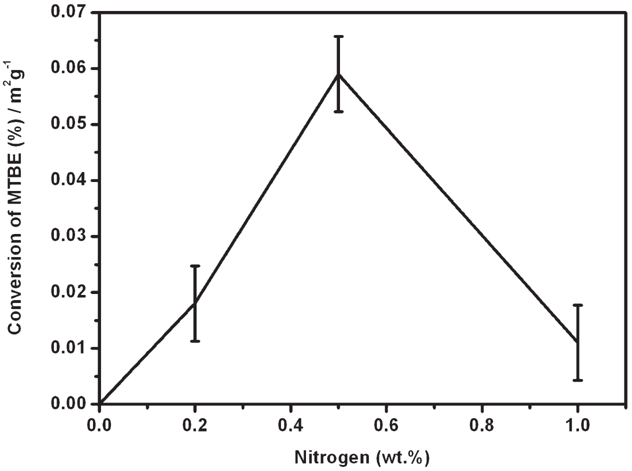

Fig. 3 Photocatalytic activity of the samples measured in single-pass reactor (space velocity ~ 4 400 h^{-1}) as a function of nitrogen-concentration normalized for surface area.

repeated preparations of different batches of samples. The error bars in Fig. 3 are derived from measurements on three different samples of each composition, prepared afresh. The observation of a pronounced optimum activity as a function of N content is noteworthy: further investigation of this effect should shed light on the overall photocatalytic mechanism. The results shown in Fig. 3 have been normalized with respect to the measured BET surface areas (Table 1) which introduces only small corrections to the raw data. Therefore, we can unambiguously attribute the observed trend in photocatalytic activity to variation in the nitrogen content, achieved in a controlled way by the novel synthetic procedure described above. The optimum performance of the 0.5 wt% N catalyst was confirmed by measurements of CO_2 production. Small quantities of intermediate products were also detected. In the case of the 0.5 wt% N catalyst these amounted to 2.8%, 0.2% and 16% of MTBE consumed for acetone, *tert*-butyl formate and acetaldehyde respectively, accompanied by very small amounts of *tert*-butyl formate.

In summary, effective *visible light active* photocatalysts have been prepared by a low-cost synthetic method that allows controllable and reproducible doping of TiO_2 with nitrogen. Maximum activity occurs at 0.5 wt% N, an interesting phenomenon that awaits further investigation. The synthetic method is well suited to scale up for the production of large quantities of material at an economic cost, thus opening the door to a variety of new uses in environmental remediation, public health protection and self-cleaning applications.

We acknowledge The Korea Science and Engineering Foundation (Grant No. M06-2004-000-10026, S.I.); the UK EPSRC (F.G., D.S.W.); King's College, Cambridge (Fellowship for A.O.); Wolfson College, Cambridge (Fellowship for F.G.).

Notes and references

1 A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, 1995, **95**, 735.
2 R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 2001, **293**, 269.
3 S. Sakthivel, M. Janczarek and H. Kisch, *J. Phys. Chem. B*, 2004, **108**, 19384.
4 S. Sakthivel and H. Kisch, *ChemPhysChem*, 2003, **4**, 487.
5 X. H. Huang, Y. C. Tang, C. Hu, H. Q. Yu and C. S. Chen, *J. Environ. Sci.-China*, 2005, **17**, 562.
6 K. Kobayakawa, Y. Murakami and Y. Sato, *J. Photochem. Photobiol., A*, 2005, **170**, 177.
7 S. Livraghi, A. Votta, M. C. Paganini and E. Giamello, *Chem. Commun.*, 2005, **4**, 498.
8 Z. P. Wang, W. M. Cai, X. T. Hong, X. L. Zhao, F. Xu and C. G. Cai, *Appl. Catal., B*, 2005, **57**, 223.
9 H. M. Yates, M. G. Nolan, D. W. Sheel and M. E. Pemble, *J. Photochem. Photobiol., A*, 2006, **179**, 213.
10 T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto and S. Sugihara, *Appl. Catal., B*, 2003, **42**, 403.
11 S. Sato, R. Nakamura and S. Abe, *Appl. Catal., A*, 2005, **284**, 131.
12 H. Irie, Y. Watanabe and K. Hashimoto, *J. Phys. Chem. B*, 2003, **107**, 5483.
13 A. Orlov, M. Tikhov and R. M. Lambert, *C. R. Chim*, 2006, **9**, 794.
14 Z. S. Lin, A. Orlov, R. M. Lambert and M. C. Payne, *J. Phys. Chem. B*, 2005, **109**, 20948.