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Facile preparation of N-doped TiO_2 at ambient temperature and pressure under UV light with 4-nitrophenol as the nitrogen source and its photocatalytic activities

Satoshi Horikoshi,*[a] Yutaro Shirasaka,[a] Hiroshi Uchida,[a] Natsuko Horikoshi[b] and Nick Serpone*[c]

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To date syntheses of nitrogen-doped TiO_2 photocatalysts ($TiO_{2-x}N_x$) have been carried out under high temperatures and high pressures with either NH_3 or urea as the nitrogen sources. This article reports for the first time the facile preparation of N-doped TiO_2 (P25 titania) in aqueous media at ambient temperature and pressure under inert conditions (Ar- and N_2-purged dispersions) with 4-nitrophenol (or 4-nitrobenzaldehyde) as the nitrogen source. The resulting N-doped P25 TiO_2 materials were characterized by UV/Vis and X-ray photoelectron spectroscopies (XPS) that confirmed the presence of nitrogen within the photocatalyst; X-ray diffraction (XRD) techniques confirmed the crystalline phases of the doped material. The photocatalytic activity of N-doped TiO_2 was assessed through examining the photodegradation of 4-chlorophenol in aqueous media and iso-propanol as a volatile pollutant under UV/Vis and visible-light irradiation. Under visible light irradiation, undoped P25 was inactive contrary to N-doped P25 that successfully degraded 95% of the 4-chlorophenol (after 10 h) and 23% of iso-propanol (after 2.5 h).

1. Introduction

Development of new methods and introduction of new technologies toward environmental sustainability poses significant challenges, particularly in Green Chemistry where noteworthy research has focused in developing new types of catalysts. Traditionally, titanium dioxide (TiO_2) is a well-recognized photocatalyst used in such applications as surface self-cleaning,[1] air purification,[2] water purification,[3] and most critically in the production of hydrogen through the water splitting process.[4] This metal oxide is readily available in nature, is chemically stable, and is highly photoactive under UV light. Historically, the successful demonstration by Fujishima and Honda[5] in 1972 that water could be decomposed photoelectrochemically with TiO_2 as one of the photoelectrodes led to a significant number of studies in the search for the Holy Grail photocatalyst that could split water into its constituent elements with a view to establish a hydrogen economy. The subsequent decade of the 1980s witnessed another principal use of this metal–oxide semiconductor as the premier photocatalyst toward the degradation of organic pollutants, in particular, and as the major component in environmental photocatalysis. Previous studies have reported on the characteristics and mechanisms of TiO_2 photocatalysis.[6]

A major problem that limits the practical applicability of this metal–oxide photocatalyst is its relatively large bandgap (*ca.* 3.2 eV for anatase; 3.0 eV for rutile), which renders this material inactive when irradiated at wavelengths longer than 387 nm (the absorption edge of anatase TiO_2), so that only UV light of shorter wavelengths can effectively activate this photocatalyst. To extend its effectiveness and responsiveness to visible-light irradiation, the last 15 years have focused on modifications of this metal oxide by incorporating dopants into its crystalline lattice.[7] Some of the reported modifications involved incorporating either cations[8] and/or anions[9] as dopants or as co-dopants into the lattice, as well as metal clusters and/or nanoparticle deposits onto the surface of the particulates.[10] For instance, fluoride modification of the TiO_2 surface was achieved in a NaF/HF solution mixture,[11] through which the fluoride ions displaced and replaced surficial hydroxyl groups bound to surface Ti^{IV} species, causing the absorption edge of F-doped TiO_2 to shift from 387 nm to 420 nm. Recent review articles by Etacheri *et al.*[12] and by Asahi and coworkers[13] have discussed at some length the various

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[a] *Department of Materials & Life sciences, Faculty of Science and Technology, Sophia University, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan. E-mail: horikosi@sophia.ac.jp, yumapa55@hotmail.co.jp, uchidah@sophia.ac.jp*

[b] *Chemical Research Center, Central Glass Co. Ltd, 2-17-5 Nakadai, Kawagoe, Saitama 350-1159, Japan. E-mail: natsuko.horikoshi@cgco.co.jp*

[c] *PhotoGreen Laboratory, Dipartimento di Chimica, Universita di Pavia, Via Taramelli 12, Pavia 27100, Italy. E-mail: nick.serpone@unipv.it*

modifications of TiO_2 to make it responsive to visible light radiation.

Nitrogen-doped titanias, $TiO_{2-x}N_x$, have been examined extensively and have been most often prepared with either ammonia or urea as the principal sources of nitrogen.[14] Both dry processes and wet processes have been employed to prepare N-doped TiO_2 and other anion-doped titanias. Dry processes have usually involved oxidation of titanium nitride, TiN, in a flow of oxygen gas at 400 to 550 °C for 1.5 h, or otherwise subjecting a dry TiO_2 powder to a NH_3/Ar gas flow at 600 °C for several hours.[14,15] Alternatively, nitridation of TiO_2 has also been achieved by subjecting the sample to a plasma of nitrogen gas or nitrogen/hydrogen mixed gases,[16,17] or else through mixing and grinding TiO_2 powders with either hexamethylenetetramine or urea in a planetary ball mill at 700 rpm for 1 h followed by calcination at 400 °C to remove residual organic substances.[18,19] Wet processes to prepare N-doped TiO_2 typically involve sol–gels formed either hydrothermally or solvothermally using a titanium source (*e.g.* $TiCl_3$, $TiCl_4$, $Ti(SO_4)_2$) and a nitrogen source (*e.g.* alkali NH_3, triethanolamine, NH_4Cl, urea, hydrazine, and guanidine hydrochloride).[13] Gas phase syntheses of N-doped titanias have also been achieved by an atmospheric pressure plasma process, and through the use of a microwave plasma torch at atmospheric pressure.[20,21]

The nature of the nitrogen species so incorporated has been the subject of some debate[12,13] because of its strong dependence on the preparative methods. Nitridation may involve various types of nitrogeneous species such as N, nitric oxide (NO), nitrogen dioxide (NO_2) at substitutional sites replacing O {represented as $(N)_O$} or at interstitial sites (denoted as $(N)_i$) in the anatase/rutile crystalline lattices,[22,23] which may lead to formation of oxygen vacancies (V_O) within the lattice. Although such species as $(N)_O$, $(N)_i$, and $(NO)_O$ in N-doped titanias have been inferred to impart effective photocatalytic activity under visible light, analyses of density of states have not been commensurate to assert such inferences.[13]

Modifications brought on TiO_2 red-shift the absorption edge from 387 nm (anatase) or 400 nm (rutile) into the visible spectral region and so $TiO_{2-x}N_x$ are expected to significantly increase their activity toward some of the practical applications noted above. Unfortunately, the methods used to incorporate the dopant into the lattice remain impractical at the industrial scale as they require heating TiO_2 to high temperatures (*ca.* 500 °C) under strong reductive conditions when employing, for example, ammonia as the N source, not to mention the long heating times especially for the commercial P25 TiO_2, well-known for its high photocatalytic activity under UV radiation; however, the photocatalytic activity of N-doped P25 so prepared decreased subsequent to the doping process.[12]

In this article we report a facile preparation of $TiO_{2-x}N_x$ using P25 titania and an alternative and effective nitrogen source, namely 4-nitrophenol (and/or nitrophenol-type compounds), which although a notorious toxic industrial dye waste[24] permits nitrogen doping to be carried out by mixing dilute concentrations of 4-nitrophenol with P25 TiO_2 in aqueous media under oxygen-depleted (Ar-purged or N_2-purged dispersions) conditions, and utilizing only UV light irradiation for a short time (<1 h). The significance of our wet preparation of N-doped P25 TiO_2, which to our knowledge has not heretofore been reported, emphasizes the important differences from previously described wet processes such as the sol–gel methods[13] because the latter do not permit direct doping in aqueous-media. Also unlike other procedures,[12,13] the present method requires only ambient temperature and pressure. The photocatalytic activity of the resulting N-doped TiO_2 was subsequently ascertained through the photodegradation of another toxic waste, 4-chlorophenol, in aqueous media and iso-propanol (IPA) as a model of volatile pollutants under both UV/Vis light and visible-light irradiation.

2. Experimental section

2.1 Preparation of N-doped TiO_2

High purity grade 4-nitrophenol was supplied by Wako Pure Chemical Ltd, whereas the P25 TiO_2 was supplied by Evonik (particle size, *ca.* 20–30 nm by TEM observations; 83% anatase and 17% rutile by X-ray diffraction; surface area, 53 $m^2\ g^{-1}$ measured by the BET method). Aqueous solutions (0.10 mM, 20 mL) of 4-nitrophenol were placed in a closed 74 mL Pyrex vessel containing TiO_2 particles (loading, 100 mg), followed by sonication for 5 min. Purging the aqueous dispersions with Ar, N_2, or O_2 (as required) was performed for 10 min using a syringe needle; experiments were also carried out under air-equilibrated conditions for comparison. UV/Vis irradiation was carried out using a Toshiba SHLS-1002A 75 W Hg lamp (irradiance, *ca.* 1.4 mW cm^{-2}; wavelength range, 310–400 nm; maximal emission in the UV at λ = 365 nm; Fig. 1). At the end of the photodegradation, the TiO_2 dispersion was centrifuged (3000 rpm for 20 min) to recover the TiO_2 powder which, subsequent to washing with deionized water, was then dried in an electric furnace.

The absorption spectra of the undoped and N-doped TiO_2 particles (in powdered form) were recorded on a JASCO V-650 UV-VIS spectrophotometer equipped with an integrating-

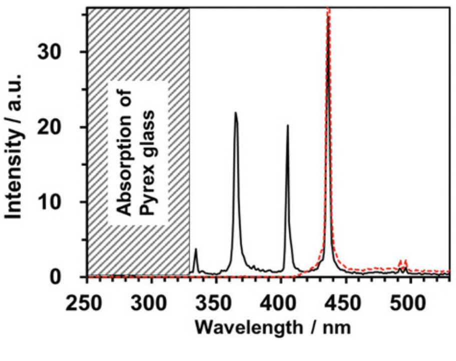

Fig. 1 UV/Vis emission spectra of the Hg lamp: solid black line, no filter; dashed red line, with UV-light cutoff filters displaying the predominant 436 nm mercury line.

sphere assembly. The N_{1s} core levels on the N-dopant were measured by X-ray photoemission spectroscopy (XPS; PHI 5000 VersaProbe II ULVAC-PHI, Inc) to ascertain nitrogen doping of the P25 TiO_2 particles from the Ar-purged or O_2-purged photodegradation of 4-nitrophenol. The integrity of the crystalline structure of the TiO_2 particles that had been treated under Ar-purged conditions was ascertained using a Rigaku X-ray diffractometer (RINT 2100) system.

2.2 Photocatalytic degradation of 4-nitrophenol

The photodegradation of 4-nitrophenol through opening of the benzene ring was monitored using a JASCO V-650 UV/VIS spectrophotometer; wavelength at 316 nm. Concentrations of NH_4^+ and NO_3^- ions formed in the photodegradation were assayed using a JASCO liquid chromatograph (HPLC) equipped with a CD-5 conductivity detector, and with a Y-521 cationic column or an I-524 anionic column.

2.3 Photocatalytic activity of N-doped P25 TiO_2

The photoactivities of the photocatalyst samples were determined by examining the photodegradation of 4-chlorophenol in aqueous media (40 mL; 0.050 mM). The solution was poured into a 74 mL Pyrex vessel containing 100 mg of either the commercial undoped P25 TiO_2 or the as-prepared N-doped TiO_2 P25 (N-P25), followed by sonication for 5 min; unless noted otherwise purging the dispersions with O_2 gas was performed for 10 min. UV/Vis irradiation of the dispersions was carried out using the Toshiba SHLS-1002A 75 W Hg lamp (Fig. 1). UV light wavelengths below 310 nm were cut-off by the Pyrex reactor, while UV light below 400 nm was cutoff with specifically designed cutoff filters supplied by Sigma Koki Co. Ltd to assess the photocatalytic activities of P25 TiO_2 and the as-prepared N-doped P25 TiO_2 in the visible spectral range. Ring-opening of benzene of the 4-chlorophenol was monitored by the decrease of the band at 280 nm using the JASCO V-650 UV-VIS spectrophotometer.

The photoactivity of the N-P25 particulates was also evaluated by examining the photodecomposition of iso-propanol (IPA; Wako Pure Chemical Industries, Ltd) as a model of volatile organic pollutants in air. The Pyrex glass batch reactor (internal diameter: 100 mm; internal height: 60 mm) with a quartz lid is illustrated in Fig. 2. The N-P25 or P25 particles were placed in a petri dish (40 mg), followed by injecting IPA (initial volume 0.8 μL, concentration was *ca.* 830 mg L^{-1} (note 1 mg L^{-1} = 1 ppm)) in the closed reactor. The system was allowed to stand in the dark for 30 min to achieve adsorption equilibration of the IPA onto the N-P25 particulates, after which the system was UV/Vis or visible-light irradiated using a Xe lamp (CX-04E) from the top of the quartz window (a Sigma Koki Co. Ltd UV cutoff filter (λ < 420 nm) was used for the visible condition). The temporal decrease of IPA concentration was periodically measured with a Shimadzu gas chromatograph (GC-2014; GL Science, Sorbitol column).

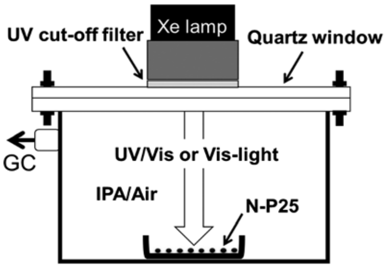

Fig. 2 Schematic of the experimental setup used for the photodecomposition of iso-propanol (IPA) using P25 or N-P25 particles under air-equilibrated conditions.

3. Results and discussion

3.1 Preparation of N-doped P25 TiO_2

UV irradiation of TiO_2/4-nitrophenol aqueous dispersions for 1 h under Ar-purged and N_2-purged conditions caused these dispersions to turn from white to a yellowish tinge (see Fig. 3), contrary to those subjected to O_2-purged and air-equilibrated conditions that remained white throughout. The components of the yellowish dispersions were subsequently filtered or centrifuged to identify the nature of the yellowish colour of the TiO_2 powders; the remaining aqueous solution phase was colourless.

Generally, the cause for the TiO_2 colour change from white to yellow is the result of doping this metal oxide with either nitrogen and/or sulphur doping consistent with earlier reports.[25] To confirm that doping had indeed occurred, the UV/Vis absorption spectra of purified and dried TiO_2 powders collected after the photodegradation of 4-nitrophenol were recorded by diffuse reflectance spectroscopy; the spectra reported as absorption spectra are illustrated in Fig. 4. The spectra of the titania sample subjected to Ar purging and N_2-purging, displayed in Fig. 4a and b respectively, show increased absorption features at wavelengths 400–600 nm, consistent with spectra reported in many earlier studies attributed to nitrogen doping of this metal oxide.[12,13,26] Treatment of the yellowish TiO_2 samples with deionized water followed by heating to 350 °C in an electric furnace showed no observable changes in colour. This demonstrates that the color change from white to yellow was not the result of adsorption of

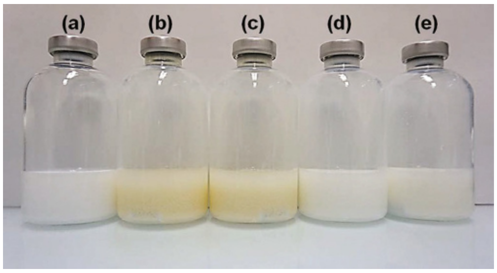

Fig. 3 Aqueous TiO_2 dispersions containing 4-nitrophenol (0.10 mM) after being subjected to UV irradiation for 1 h (a) control dispersion (air-equilibrated but not UV irradiated), and after being (b) Ar-purged, (c) N_2-purged, (d) O_2-purged, and (e) air-equilibrated.

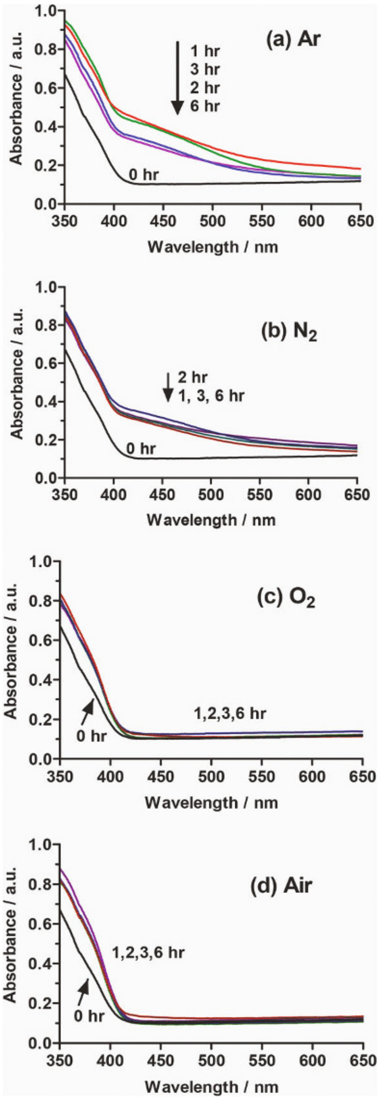

Fig. 4 Absorption spectra of dried P25 TiO_2 powders collected from dispersions UV irradiated for 0, 1, 2, 3 and 6 h under (a) Ar-purged, (b) N_2-purged and (c) O_2-purged atmospheres, and (d) in air-equilibrated conditions subsequent to the photodegradation of 4-nitrophenol (0.10 mM).

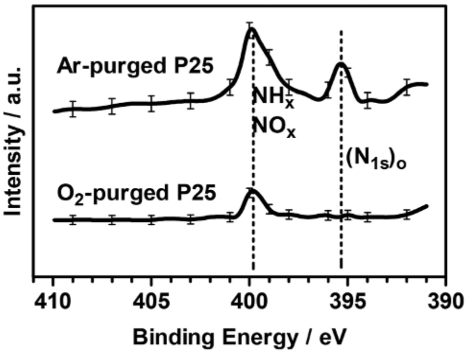

Fig. 5 XPS spectra of purified and dry P25 TiO_2 particles recovered from the photodegradation of 4-nitrophenol (0.10 mM) in aqueous media under Ar-purged and O_2-purged conditions; vertical bars denote the noise levels of the spectra, while the solid lines express the averaged signals.

4-nitrophenol to the surface of TiO_2, but from nitrogen doping[26] that typically leads to formation of oxygen vacancies and thus colour centres as described in earlier studies by Kuznetsov and Serpone.[27–32] By contrast, the dispersions subjected to O_2-purging and air-equilibrated conditions showed no absorption features in the same wavelength range of 400 to 600 nm (see Fig. 4c and d).

Further confirmation of nitrogen doping of the Ar-purged yellowish P25 TiO_2 sample was obtained from an examination of the respective XPS spectra illustrated in Fig. 5, which show a peak at a binding energy of *ca.* 396 eV and confirms nitrogen doping of the TiO_2 particles. In line with previous studies,[13,26,33] we attribute this peak to formation of Ti–N bonds wherein the oxygen is substituted by nitrogen in the metal–oxide crystalline lattice as per the calculations of Asahi and coworkers[13] who placed the binding energy of substitutional $(N_{1s})_O$ at 395.70 ± 0.17 eV. However, as pointed out by these authors, assignment of the binding energies of N-doped TiO_2 remains a matter of some debate. A similar peak at 396 eV was also observed in the N_2-purged P25 sample. The XPS spectrum of the O_2-purged P25 showed no peak at 396 eV within the experimental noise. The asymmetric broad XPS peak at *ca.* 400 nm for the Ar-purged P25 sample likely consists of two overlapping signals that might due to N_{1s} from NH_x and NO_x species at the surface as argued by Asahi and coworkers.[13] A similar signal was observed in the XPS spectrum of the O_2-purged sample, albeit of much lower intensity and which we tentatively attribute to NO_x species owing to the oxidative conditions under which the sample was subjected to.

Possible changes in the crystalline structure of P25 TiO_2 resulting from nitrogen doping were investigated using the XRD technique. The original XRD peaks of the anatase phase of P25 TiO_2 particles displayed no change in intensity subsequent to nitrogen doping (Fig. 6). The lattice parameters (*a*/*c* axis) of P25 titania and N-doped P25 TiO_2 were 0.3790 nm/0.9508 nm (P25) and 0.3709 nm/0.9509 nm (N-P25) for anatase, and 0.4598 nm/0.2959 nm (P25) and

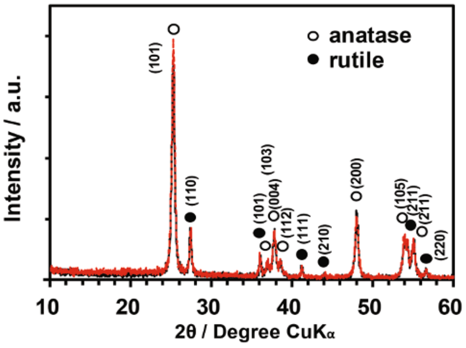

Fig. 6 X-ray diffraction patterns for untreated P25 TiO_2 particles (black dashed curve), and N-doped P25 particles (solid red curve).

0.4597 nm/0.2959 nm (N-P25) for rutile. The crystallite sizes from the XRD peaks of anatase(101)/rutile(110) were estimated as 26 nm/93 nm (P25) and 26 nm/95 nm (N-P25). It is noteworthy that when using urea as a nitrogen source for N doping of TiO_2, structural changes occur owing to the high temperatures required for the preparation process.[26] The advantage of using the N-doping process reported herein is that there are no changes to the crystallite phase.

Fig. 7 reports the time course of the TiO_2-assisted UV-induced photodegradation of 4-nitrophenol under inert (Ar-purged) and oxidative (O_2-purged) conditions. Under inert conditions (Fig. 7a), the degradation of 4-nitrophenol was delayed by *ca.* 45 min before the concentration of the phenol began to decrease, albeit very slowly accounting for only ~13% of benzene ring opening as confirmed by UV/vis spectroscopy (λ = 317 nm) after 3 h of UV irradiation. Concomitantly, formation of NO_3^- and NH_4^+ ions also began to occur after the 45 min delay, resulting in a combined concentration of nitrate and ammonium ions of 17% formed at the 3 h mark.

By comparison, benzene ring opening proceeded much more rapidly from the start of UV irradiation in O_2-purged TiO_2 dispersions, with 4-nitrophenol being fully transformed within 2 h of irradiation (Fig. 7b). A significant difference with the Ar gas purging conditions was the rapid formation of NO_3^- ions in the presence of O_2. After 1 h of UV irradiation, 64% of all the nitro groups were transformed into NO_3^- ions, while only *ca.* 5% of NH_4^+ ions formed after 3 h under O_2-purged conditions.

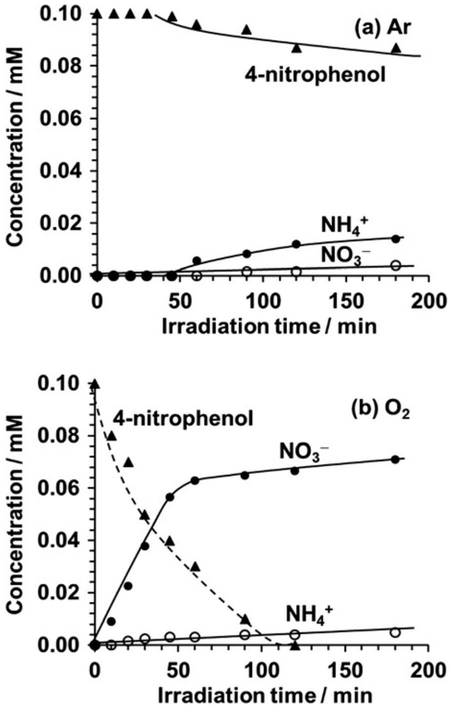

Fig. 7 Formation of NH_4^+ and NO_3^- ions, and opening of the phenyl ring during the UV-assisted photocatalytic degradation of 4-nitrophenol in the presence of P25 TiO_2 particulates under (a) Ar-purged and (b) O_2-purged conditions.

3.2 Nitrogen doping of P25 TiO_2 under various conditions

Changes in the UV/Vis spectra of purified and dried TiO_2 powders observed following the photocatalytic degradation of 4-nitrophenol at three different concentrations (0.1 mM; 1.0 mM; 10.0 mM) in Ar-purged dispersions are displayed in Fig. 8a. Absorption at wavelengths longer than 400 nm increased somewhat with increase in concentration of the nitrophenol. A similar phenomenon was observed under N_2-purged conditions. On the other hand, although there were no significant changes in the spectrum at 0.10 mM under O_2-purged conditions, there was a significant change in absorption in the visible at the higher concentrations (Fig. 8b; see also below).

Fig. 9 illustrates the visual colour changes of the aqueous dispersions after the photodegradation reaction. The TiO_2 powder became significantly yellow after the degradation at the highest concentration of 4-nitrophenol. Where the concentration of the nitrophenol was 1.0 mM, the change in colour {bottle (a) to bottle (c)} was significantly less compared to observations where the dispersions were Ar-purged. However, at the higher concentration (10.0 mM), the colour of the dispersion was rather similar to the colour under Ar-purged conditions. Organic compounds ultimately breakdown into CO_2 gas in TiO_2-photocatalyzed reactions and thus require dissolved oxygen whose concentration tends to decrease as the degradation proceeds. In the degradation of 10.0 mM of 4-nitrophenol, the dissolved oxygen is likely depleted during the early stages of the degradation, and at some point the atmospheric conditions will then be similar to those under inert conditions (Ar-purged and N_2-purged).

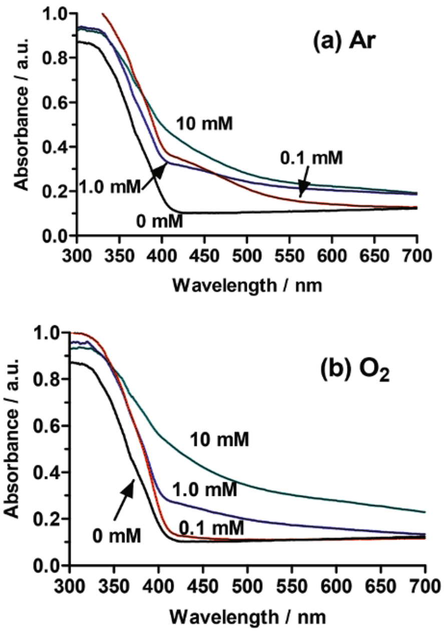

Fig. 8 Absorbance spectra of purified and dried TiO_2 powders from (a) Ar-purged and (b) O_2-purged dispersions after the photodegradation of 4-nitrophenol at three different concentrations (0.10 mM, 1.0 mM, and 10.0 mM) under UV irradiation for 0 and after 1 h.

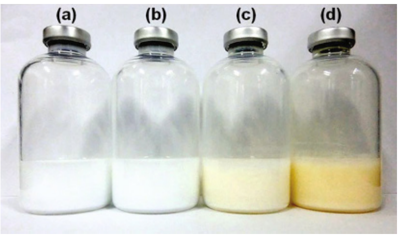

Fig. 9 Aqueous dispersions containing TiO_2 and 4-nitrophenol after the photodegradation for 1 h at various concentration in the nitrophenol: (a) control (no UV irradiation; 0.10 mM), (b) 0.10 mM, (c) 1.0 mM and (d) 10.0 mM under O_2-purged conditions.

3.3 On the origin of the N dopant in N-doped titania

The source of nitrogen in the N-doped P25 titania sample is the nitro group in 4-nitrophenol. To test this hypothesis, the photodegradation of phenol (no nitro group) was carried out under Ar- and N_2-purged conditions, conditions otherwise similar to those used for the nitrophenol. Neither the color nor the absorption spectrum of TiO_2 changed after the degradation of phenol. Furthermore, photodegradation of other nitro or amine compounds soluble in aqueous media such as nitroethane ($CH_3CH_2NO_2$, 0.10 mM) and urea (NH_2CONH_2, 0.10 mM) were also tested under Ar-purged conditions. Again, neither the colour nor the absorption spectrum of TiO_2 displayed any changes, clearly indicating that under the conditions used herein not all nitro or amine-type compounds can dope TiO_2 with nitrogen.

The degradation of 4-aminophenol ($NH_2C_6H_3OH$; 0.10 mM) was also tested as a possible source of N dopant to prepare N-doped P25 under otherwise identical conditions; no changes in colour or absorption spectrum were observed. By contrast, when degrading 4-nitrobenzaldehyde ($NO_2C_6H_4CHO$; 0.10 mM) or 2,4-dinitrophenol ($N_2O_5C_6H_3OH$; 0.10 mM) under the Ar-purged conditions, the resulting TiO_2 powders adopted a yellow colour and the absorption spectrum displayed significant absorption at wavelengths longer than 400 nm, in line with those observed for the 4-nitrophenol. From these observations, we infer that both a phenyl ring and a nitro group are required components to N-doped titania under our experimental conditions.

To the extent that the products from the photodegradation of 4-nitrophenol might be the source of the N dopant, we tested both NH_4^+ and NO_3^- ions as the possible sources. Accordingly, both an NH_4Cl solution (0.10 mM) and NH_4NO_3 solution (0.10 mM) were used as the possible sources when mixed with P25 TiO_2 in O_2-purged and Ar-purged dispersions. Results also showed no change in colour of the titania, and no absorption in the visible spectra range after 1 h of UV irradiation. In summary then, to dope TiO_2 with nitrogen, some reactant with a nitrophenyl-type backbone is necessary and the photodegradation needs to be carried out under O_2-free conditions.

3.4 Proposed mechanism of nitrogen doping

Mechanistic details of photocatalytic degradation processes involving TiO_2 particles have been described at some length in many review articles[34–37] (and references therein). In the present context, the overall reaction that leads to N doping of the P25 titania sample can simply be described by eqn (1):

$$TiO_2 + h\nu + 4\text{-}NO_2PhOH \rightarrow TiO_{2-x}N_x \tag{1}$$

Although the available data are limited, it is nonetheless worth speculating briefly on some relevant steps that lead to the degradation of the nitrophenol through which the N-doped TiO_2 is formed. Absorption of UV light of energy greater than the bandgap (*ca.* 3.2 eV; $\lambda > ca.$ 387 nm) generates electron/hole pairs (eqn (2)), followed by various steps in which the holes (h^+_{VB}) are ultimately trapped by OH^- ions (or by H_2O) at the particle surface to yield $^\bullet OH$ radicals (and H^+; eqn (3a)). These are the major oxidizing radicals in the oxidative degradation of 4-nitrophenol (eqn (3b)) that lead to phenyl ring opening followed by denitration and formation of NH_4^+ and NO_3^- ions, and ultimately to CO_2. Concomitantly, valence band holes can, in principle, oxidize directly the nitrophenol to yield similar products, although this path (eqn (3c)) is likely less important.

UV irradiation

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-_{CB} + h^+_{VB}) \tag{2}$$

Valence band hole path (O_2-purged and air-equilibrated dispersions)

Major path

$$h^+_{VB} + OH_S^-(H_2O)_S \rightarrow {}^\bullet OH_S\ (+H^+) \tag{3a}$$

$$\begin{aligned} {}^\bullet OH + 4\text{-}NO_2PhOH &\rightarrow \text{phenyl ring opening} \\ &\rightarrow CO_2, NH_4^+, NO_3^- \end{aligned} \tag{3b}$$

Minor path

$$h^+_{VB} + 4\text{-}NO_2PhOH \rightarrow \text{intermediates} \rightarrow CO_2, NH_4^+, NO_3^- \tag{3c}$$

Conduction band path (O_2-purged and air-equilibrated dispersions)

Major path

$$e^-_{CB} + O_2 \rightarrow O_2^{-\bullet} \tag{4a}$$

$$O_2^{-\bullet} + H^+ \rightarrow HOO^\bullet \tag{4b}$$

$$\begin{aligned} HOO^\bullet + 4\text{-}NO_2PhOH &\rightarrow \text{phenyl ring opening} \\ &\rightarrow CO_2, NH_4^+ \ll NO_3^- \end{aligned} \tag{4c}$$

Minor path

$$e^-_{CB} + 4\text{-}NO_2PhOH \rightarrow \text{intermediates} \rightarrow CO_2, NH_4^+, NO_3^- \tag{4d}$$

In Ar- and N_2-purged dispersions subsequent to eqn (2)

Major path

$$e^-_{CB} + h^+_{VB} \rightarrow \text{recombination} \tag{5a}$$

Minor path

$$e^{-}{}_{CB} + 4\text{-}NO_2PhOH \rightarrow \text{intermediates} \rightarrow CO_2, NH_4{}^{+} > NO_3{}^{-} \quad (5b)$$

$$h^{+}{}_{VB} + OH_S{}^{-}(H_2O)_S \rightarrow {}^{\bullet}OH_S\ (+H^{+}) \quad (5c)$$

$${}^{\bullet}OH + 4\text{-}NO_2PhOH \rightarrow \text{intermediates} \rightarrow CO_2, NH_4{}^{+} > NO_3{}^{-} \quad (5d)$$

In O_2-purged and air-equilibrated dispersions, the dioxygen molecules react with conduction band electrons ($e^{-}{}_{CB}$; eqn (4a)) to yield superoxide radical anions ($O_2{}^{-\bullet}$), which on protonation generate the hydroperoxyl radicals (${}^{\bullet}OOH$; eqn (4b)), and with the ${}^{\bullet}OH$ radicals (eqn (3b)) subsequently react with 4-nitrophenol (eqn (4c)) leading to phenyl ring opening and formation of CO_2, together with $NH_4{}^{+}$ and $NO_3{}^{-}$ ions with the latter in significant excess under these conditions. Direct attachment of the conduction band electrons onto the phenyl ring of the nitrophenol under these conditions is yet another possible path, albeit a minor one (eqn (4d)).

By contrast, in Ar-purged and N_2-purged dispersions, the major path is electron/hole recombination (eqn (5a)), while a minor path involves direct attack of the 4-nitrophenol by electron attachment onto the phenyl ring (eqn (5b)), followed by formation of intermediates and finally CO_2 and the ionic species, but with significantly lower yields. We further hypothesize that during the process occurring under inert conditions, ${}^{\bullet}OH$ radicals are also formed to some extent (eqn (5c)) and oxidize the nitrophenol to its ultimate degradation (eqn (5d)).

3.5 Photocatalytic activities of the as-prepared N-doped P25 TiO_2

Most studies that examine the photocatalytic activities of metal–oxide photocatalsts, in general, and TiO_2, in particular, use the photodegradation of common dyes (*e.g.* methylene blue and rhodamine-B) because it is a facile and rapid spectroscopic method. However, such a method is to be discouraged because the dyes also absorb significantly in both the UV and visible spectral regions so that photosensitization of the metal oxide by the excited dyes can also occur concurrently with the TiO_2-assisted photodegradation.[38–43] Accordingly, we assessed the photocatalytic activity of the as-prepared N-doped P25 photocatalyst, and for comparison also undoped P25 titania, by investigating the photodegradation of 4-chlorophenol (0.050 mM) in aqueous media under both UV/Vis and visible light irradiation and under otherwise similar conditions. Results from the UV/Vis irradiation displayed in Fig. 10a reveal that both undoped TiO_2 and N-doped titania degrade the chlorophenol by nearly identical (within experimental error) zero-order kinetics in less than 3 h. By comparison, under visible light irradiation (Fig. 10b) the undoped TiO_2 is completely inactive, while the N-doped TiO_2 degrades the chlorophenol by zero-order kinetics, albeit more slowly necessitating 10 h of irradiation for 95% degradation. Thus, it is possible to degrade organic pollutants in aqueous media using N-doped TiO_2 prepared under ambient temperature and pressure with only visible light irradiation of the N-doped metal oxide.

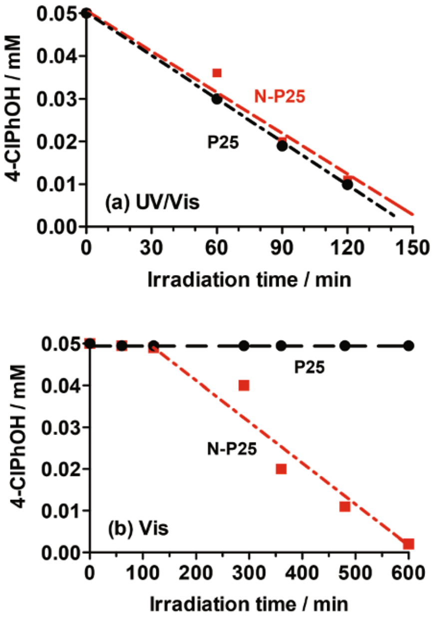

Fig. 10 Time course of the decrease of concentration during the decomposition of 4-chlorophenol (4-ClPhOH; 0.050 mM) in aqueous dispersions in the presence of commercial P25 titania or N-doped P25 TiO_2 under O_2-purged conditions: (a) UV/Vis light irradiation, (b) visible light irradiation.

After the 10 h of visible light irradiation under the conditions used (see Fig. 11), the yellow colour of N-doped TiO_2 decreased in intensity that was subsequently confirmed by the absorption spectra reported in Fig. 11, which compares the absorption spectrum of the N-doped P25 before and after the photodegradation of 4-chlorophenol under O_2-purged conditions. It is worth pointing out that the spectral features seen at wavelengths longer than 400 nm (Fig. 4a, b, 8 and 11) are typical of visible-light-active TiO_2s doped with anions and/or cations, and originate from the formation of oxygen vacancies

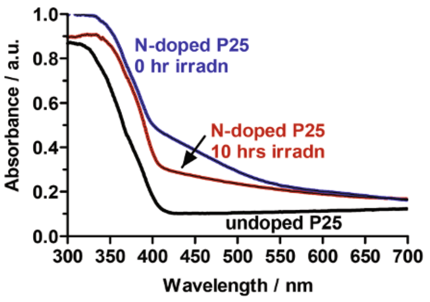

Fig. 11 Absorption spectra of undoped P25 TiO_2 powders, and N-doped P25 TiO_2 powders before (0 h) and after 10 h into the photodegradation of 4-chlorophenol in O_2-purged aqueous media under visible light irradiation.

resulting ultimately in the formation of colour centres (*e.g.*, F and/or Ti^{3+}).[29,30,44–46]

The broad absorption envelope from 400 nm to *ca.* 550 nm in Fig. 11 decreased in intensity after the 10 h period. A possible explanation would suppose that some of the N dopant atoms were exchanged with the dissolved oxygen during the photocatalytic reaction. Future studies will be undertaken to account for this inference through an examination of the effect of aging by repeated degradation of the chlorophenol, together with XPS experiments with Ar^+-ion sputtering to confirm the location of the N dopant either within the lattice and/or at the surface or sub-surface.

The photoactivity of N-P25 under both UV/Vis and visible light irradiation was further compared with that of undoped P25 using the degradation of iso-propanol (IPA) as our model system for air pollutants (Fig. 12). Approximately 44% of IPA adsorbed to the P25 TiO_2 surface compared to the initial IPA concentration (830 mg L^{-1}); surface adsorption of IPA to N-P25 amounted to *ca.* 43%. There was no significant difference when comparing the adsorption between commercial P25 and the as-prepared N-P25.

The extent of degradation of IPA was 36% and 24% in the presence of P25 and N-P25 systems, respectively, under UV/Vis irradiation for 150 min, which yielded 166 mg L^{-1} and 100 mg L^{-1} of acetone for P25 and N-P25, respectively (Fig. 12a). Evidently, under UV/Vis irradiation the photoactivity of the N-P25 system was lower than that of the undoped P25 system. By contrast, under visible-light irradiation conditions (Fig. 12b), the photodecomposition rates of IPA were 0% (P25) and *ca.* 23% (N-P25) after 150 min; the latter yielded *ca.* 60 mg L^{-1} of acetone.

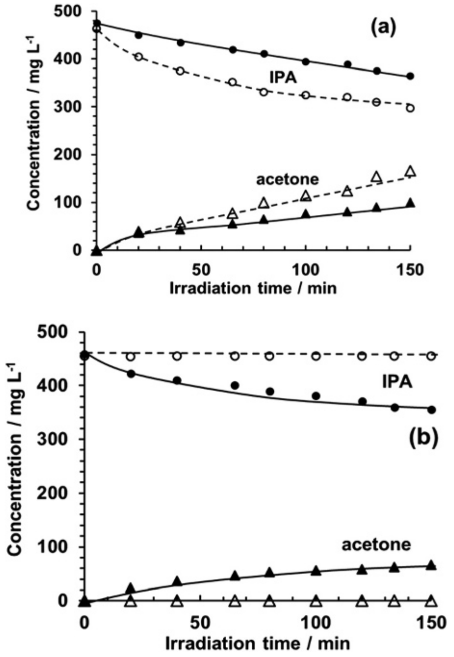

Fig. 12 Temporal decrease of the concentration of IPA and increase in the amount of acetone produced by photocatalytic degradation of IPA in the presence of P25 and N-doped P25 powders under (a) UV/Vis and (b) visible-light irradiation conditions. Data for N-P25: closed circles and triangles; data for P25: open circles and triangles.

The above results thus demonstrate a successful visible-light-driven degradation of both aqueous pollutants (4-chlorophenol) and volatile organic compounds (iso-propanol) when using N-P25.

4. Concluding remarks

The present study has demonstrated, for the first time, that nitrogen doping of a metal–oxide semiconductor photocatalyst, such as P25 TiO_2, can be achieved under ambient temperature and pressure through the photodecomposition of a 4-nitrophenyl-type compound (4-nitrophenol or 4-nitrobenzaldehyde) in oxygen-free aqueous media to yield the visible-light-active N-doped TiO_2, a process that can easily be applied at the industrial scale. The resulting $TiO_{2-x}N_x$ system can be used to degrade harmful organic pollutants (aqueous 4-chlorophenol, and the volatile iso-propanol) utilizing only visible-light irradiation, under which P25 TiO_2 is completely inactive.

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