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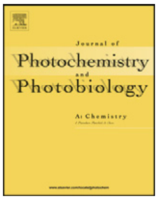

A comparative study of two techniques for determining photocatalytic activity of nitrogen doped TiO_2 nanotubes under visible light irradiation: Photocatalytic reduction of dye and photocatalytic oxidation of organic molecules

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ABSTRACT

Nitrogen-doping (N-doping) is a popular strategy for promoting the absorption of visible light in TiO_2 and other photocatalysts. We have grown TiO_2 nanotubes onto non-conducting Pyrex in a one step process via single layer titanium films. In an attempt to improve the self-cleaning ability of vertically aligned TiO_2 nanotube arrays under visible light irradiation we have doped them with nitrogen and tested the resulting nanotube films by two representative test methods. The first method is an established dye-test which is typically used as a “quick-and-dirty” screening for activity. The second method is the gas-phase oxidation reaction of CO-oxidation and methane. The encouraging results of the dye tests are in conflict with the discouraging results of the gas-phase tests. The fact that the dye test gives a “false positive” underscores the dangers of extrapolating photocatalytic performance results from dye decoloration tests to more difficult redox reactions such as hydrocarbon mineralization.

1. Introduction

TiO_2 nanotubes (NT) have received a lot of attention because of their photoelectrochemical activity [1] and photocatalytic performance [2–4]. TiO_2 NT films exhibit a significantly enhanced photocurrent and a higher photocatalytic activity compared with the bulk/powder TiO_2 films [5]. This enhancement results from the special infrastructure of the nanotube array, which is favorable for the diffusion of intermediates and the reduced deactivation of the photocatalyst in photocatalytic reactions such as self-cleaning [6,7], dye-sensitized solar cell [8] and water-splitting [9]. However, as with traditional TiO_2 thin films, photocatalytic reactions do not proceed under visible light illumination due to the large band gap of TiO_2 NT (3.2 eV for anantase). Some studies have reported that anion-doped TiO_2 NT showed photocatalytic activities in the visible region [10–12]. However these samples were formed on top of titanium foils. Therefore, a ‘bi-layer’ Ti film scheme or FTO coating was adopted for making optically transparent TiO_2 NT films [1,13]. This technique, however, yields samples with a bulk TiO_2 (or FTO) layer as well as the desired TiO_2 NT layer, which obscures characterization of the TiO_2 NT film properties. It has been reported that anodization of single-layer titanium films on top of glass substrates was unsuccessful as the metal layer in contact with the electrolyte surface was rapidly etched away, thus breaking electrical contact with the submerged portion of the film undergoing anodization before nanotubes were formed [13]. Recently, we were able to overcome this problem by optimizing the contact geometry allowing us to grow the TiO_2 NT directly onto Pyrex glass in one step [6,7].

Mills et al. developed an indicator ink providing a rapid method for assessing the possible activity of photocatalytic thin films [14]. The indicator ink is comprised of an aqueous hydroxyl ethyl cellulose (HEC) polymer solution containing glycerol, acting as the sole sacrificial electron donor and the redox dye, resazurin (Rz). Reduction of the resazurin (Rz) to resorufin (Rf) results in a color change which can be quantified using a standard spectrophotometer. Therefore, by following the color change of the stained photocatalyst as it is excited with light, one may monitor the reduction of Rz (and the concurrent oxidation of glycerol) [15]. It must be noted, however, that the reduction of the dye might be more facile (have faster kinetics) than that of O_2 or H_2O (generally the relevant oxidants in self-cleaning reactions) and firm conclusions about general self-cleaning performance cannot be based *only* on a dye test as we shall see [25]. Perhaps, the dye test can be used an initial indication as to whether or not the photocatalyst is active, but it cannot stand alone.

We have developed μ-reactors to investigate nano-scale heterogeneous catalysts and photocatalysts. The advantage of using a μ-reactor is that very small volumes of gas and catalysts can be

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handled at a time, making the response very fast. Under typical experimental conditions, the total gas flow through the reaction zone is around 6×10^{15} molecules s^{-1}, corresponding to a gas residence time in the reaction zone of about 1 s. The details of the fabrication process are explained in previous publications [16,17,26].

In this study, we have prepared visible light activated TiO_2 nanotubes via nitrogen-doping (N-TNT). These N-TNTs were coated onto non-conducting Pyrex via single layer titanium films in a one step process [6,7]. We have compared two test methods for N-TNT under visible light irradiation: photocatalytic reduction of Rz dye and photocatalytic oxidation of CO and CH_4.

2. Materials and methods

Titanium films (c.a. 400 nm thick) were deposited on Pyrex lids (20 mm × 16 mm × 1 mm) via EBPVD (electron beam physical vapor deposition). Vertically aligned transparent TiO_2 nanotube arrays were formed on the Pyrex lids by potentiostatic anodization at 10 V using the "bottom contact" one-step method [7]. The bottom contact anodization technique is well suited for this work since it allows TiO_2 nanotubes to be grown directly on *non-conductive* supports such as the Pyrex lids. A teflon-coated titanium wire was used in order to prevent evolution of oxygen which could result in local oxidation of the titanium and thus a premature loss of electrical contact. The electrolyte was a mixture of 0.3 wt.% NH_4F (98%, ACS reagent, Sigma–Aldrich) and 2 vol.% DI water in ethylene glycol (Reagentplus®, ≥99%, Sigma–Aldrich). All preparations were performed at room temperature (298 K). Prior to anodization, the samples were cleaned with acetone and ethanol followed by a deionized (D.I.) water rinse. The anodization was performed using a two-electrode cell with the titanium film as the working electrode and carbon paper as the counter electrode. The anodization was stopped once the current density of the electrode reached zero. This took about 1.5 h. After anodization, TiO_2 NT films were cleaned by sonication for 5 min. To convert the amorphous TiO_2 NT into anatase TiO_2 NT, the pure TiO_2 NTs were calcined at 400 °C for 2 h in air (30 ml/min) and the N-doped TiO_2 NT at 400 °C in gaseous NH_3 (23 ml/min). No structural damage was observed after cleaning, annealing and doping.

X-ray photoemission spectroscopy (XPS) was used to investigate Ti 2p and O 2p core levels of the N-TNTs. For all the XPS data obtained, the Al Kα peak at 1486.68 eV was used to probe the sample. An acceleration voltage of 15,000 V, a current of 0.0067 A, and a pass energy of 50 eV were used.

For the field emission scanning electron microscopy (FESEM), a QUANTA 200 FEG MKII FESEM was used at CEN (Center for Electron Nanoscopy), DTU. The samples were contacted to a metallic sample holder using conductive silver paint. Subsequently, a 3 nm layer of gold was sputter deposited on top of the samples.

The crystallinity of the sample was investigated using a Philips X'pert Pro X-ray diffractometer operating with copper radiation (Cu K_α) filtered with a nickel foil. A Varian Cary 1E UV–visible spectrometer was used to record UV–vis spectroscopy.

The typical indicator ink used in this work contained 3 g of a 1.5 wt.% aqueous solution of hydroxyethyl cellulose (HEC), 0.3 g of glycerol and 4 mg of the redox dye, resazurin (Rz) (11). The samples were coated with the indicator ink by spin-coating (2000 rpm for 10 s) followed by drying at 70 °C for 30 min and the optical absorption was measured every 5 s.

The light source used was a Luxeon™ Star/O LED (LXHL-NWE8, 45 lm at 350 mA) with Monochromat filter (Carlzeiss) and 420 nm cutoff filter (Newport, FSR-GG420). Irradiance was measured by a NIST traceable spectroradiometer. After the light had passed through the optical filters, the maximum light intensity was moderate: 3.95 mW/cm^2 (430–480 nm).

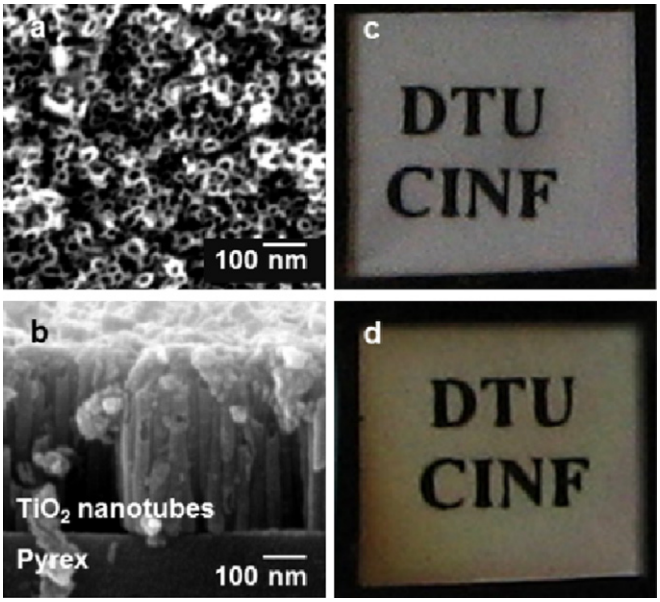

Fig. 1. Typical FESEM images of the top (a) and cross-sectional (b) views for the N-TNT on Pyrex substrate. Digital images of pure TiO_2 NT coated window (c) and N-TiO_2 NT coated window (1 cm × 1 cm).

3. Results and discussion

Top and side-view FESEM images of N-TiO_2 NT on a Pyrex substrate are shown in Fig. 1a and b, respectively. The average inner pore diameter is about 20 nm and wall thickness is approximately 10 nm. Viewed from the cross-sectional SEM images, the samples look thin and elongated; from the top, they are hollow and highly ordered. The N-TiO_2 NTs are about 400 nm in length. Fig. 1c shows a photograph of pure, undoped TiO_2 NTs which are clear and transparent, showing the DTU logo on a piece of paper placed underneath the Pyrex glass prior to anodization. In contrast to Fig. 1c, the N-TiO_2 NT window has a pale yellow color (Fig. 1d). This pale yellow color change corresponds to the changes apparent in the UV–vis absorption spectra shown in Fig. 2a.

The UV–vis absorption spectra of pure TiO_2 NT and N-TiO_2 NT are compared in Fig. 2a. It is apparent that the optical absorption in the visible region increased with the addition of nitrogen atoms and the absorption edge shifted to higher wave numbers (red-shift). This result indicates that nitrogen doping can promote visible light absorption, which is a pre-requisite for photocatalytic activity under visible light. This observation is consistent with other nitrogen-doped TiO_2 film studies [18]. Since the films being examined here are fairly thin, fringing occurs due to the Fabry-perrot effect. This is produced by the constructive and destructive interference of multiplied, reflected light in the etalon, formed by the substrate/thin film interface. Because the light is swept towards shorter wavelengths, the result is that the absorbance display oscillations are superposed onto the real spectrum with decreasing pitch. The high degree of homogeneity of the film caused a particular prevailing fringing effect. XRD data of Fig. 2b shows that the as-prepared TiO_2 NTs was amorphous. From these XRD patterns, it is observed that there is a significant growth of the anatase phase ($2\theta = 25.3°$) for pure TiO_2 NT after calcination at 400 °C for 2 h in air (30 ml/min) and for N-TiO_2 NT where gaseous ammonia (23 ml/min) was selected in place of air. The peak is assigned to the (1 0 1) planes of anatase (A) phase.

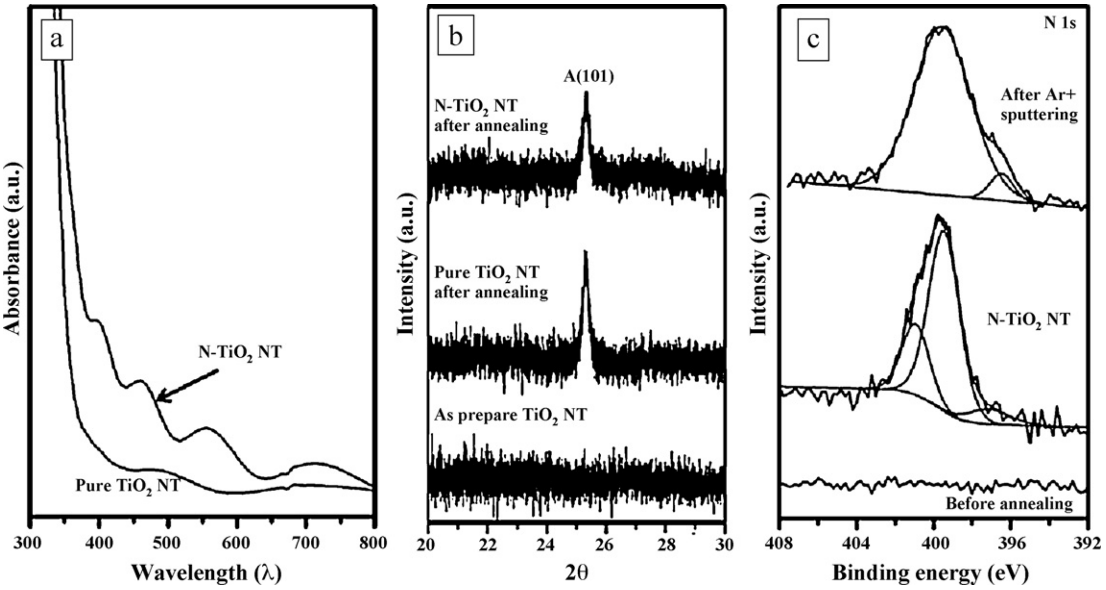

Fig. 2. UV–vis absorbance spectra of (a) pure TiO_2 NT and N-doped TiO2 NT; (b) XRD patterns of TiO_2 NT as prepared, pure TiO_2 NT after calcination and N-doped TiO_2 NT after calcination; (c) N 1s XPS of pure TiO_2 NT, N-doped TiO_2 NT as-prepared and N-doped TiO2 NT after Ar+ sputtering for 6 min.

To investigate nitrogen states in N-doped TiO_2 NT, the N 1s core levels of the samples were measured with X-ray photoemission spectroscopy (XPS) as shown in Fig. 2c. The XPS data confirms a successful incorporation of nitrogen into the TiO_2. The N 1s emission is very broad implying the presence of more than one form of nitrogen. Inspection of the N 1s signal indicates a presence of low and high binding energy (BE) components. The high BE components (at 401.0 eV and 399.5 eV) correspond to a high oxidation state of nitrogen, which can be explained by a formation of nitric oxide-like material. The lower binding energy component at 396.5 eV corresponds to a lower oxidation state of nitrogen, which is thought to be responsible for photocatalytic activity of N-doped TiO_2 NT in the visible region [19–21]. Ar^+ sputtering reveals a much clearer peak at 396.5 eV. The observation of a N 1s core level at 396.5 eV supports the conclusion that the nitrogen should be present as a N–Ti–O linkage. In most cases, a peak at 396–397 eV was detected and attributed to N-doping. However XPS data did not provide confirmation of substitutionally doped nitrogen concentration due to the poor signal:noise ratio. It is well known that quantification and chemical analysis of small concentrations of N in TiO_2 is far from trivial [22]. Synchrotron-based XPS could provide a possible solution to this issue.

Indicator ink coated pure and N-doped TiO_2 NT windows were evaluated by monitoring the reduction reaction of the Rz dye upon irradiation with visible light ($420\,nm < \lambda < 500\,nm$) as shown in Fig. 3. N-doped samples (Fig. 3a) bleach significantly faster than pure, undoped samples (Fig. 3b). Upon excitation of N-doped TiO_2 NT windows with visible light, the sacrificial electron donor (SED) acts as a hole-sink to prevent electron–hole recombination. The photogenerated electrons consequently irreversibly reduce the blue redox resazurin (Rz) dye to its pink coloured form, resorufin (Rf) as shown in Fig. 3c [23]. There were less notable peak changes in the pure TiO_2 NT window. Perhaps injection of electrons from the LUMO of the (photo excited) Rz molecule into the CB of the TiO_2 leaves the Rz oxidized (possibly as simply Rz^+) which apparently does not absorb at 600 nm.

Various mechanisms have been proposed to explain visible light activity of N-doped TiO_2. Asahi et al. [19] proposed that N 2p acceptor states contribute to the band gap narrowing by mixing with O 2p states. However, by means of spin-polarised DFT calculations Di Valentin et al. [24] found that nitrogen causes a significant change in the absorption spectrum of TiO_2 and showed that the N 2p orbitals are localized above the top of the O 2p valence bands (interband level). Although the above previous studies addressed some aspects of N-doped TiO_2, detailed mechanisms are still limited. In order to investigate the visible light excitation of N-doped TiO_2 NT films, synchrotron photoemission would perhaps be a solution.

Clearly, N-doping makes the TiO_2 NT films bleach resazurin under visible light, but in order to make sure that visible light activity carries over for other (non-dye) reactions we also tested the samples using our previously developed μ-reactors [17]. The μ-reactor has proven itself to be a useful tool for testing gas-phase photo-oxidation reactions [26,27]. Using CO-oxidation and methane oxidation as probe reactions we compared undoped and N-doped TiO_2 NT samples under both UV and visible light. The results are summarized in Table 1.

The undoped nanotubes are vastly superior to the N-doped nanotubes under UV illumination as evidenced by the data in Table 1. For CO-oxidation, the undoped samples are 30 times more active than N-doped nanotubes while for CH_4-oxidation the difference is roughly 7 times. Under visible light, the undoped nanotubes loose a factor $\sim$420 with respect to the UV level for CO-oxidation and for CH_4-oxidation, the activity is not measurable. The N-doped tubes suffer less from the switch to violet light loosing “only” a factor 28 for CO-oxidation and 11 for CH_4-oxidation. Note, however, that the external quantum efficiency under visible light is *very* low regardless of doping and that in the case of CO-oxidation the undoped nanotubes are at least as good as the N-doped nanotubes.

In short: while the undoped TiO_2 NT samples are active under UV illumination (and essentially inactive in visible as expected) the N-doped TiO_2 NT samples showed much decreased activity under UV illumination and are also essentially inactive in visible light.

To understand the discrepancy between the dye-results and the mineralization-results it is useful to keep in mind three key observations:

(1) Under UV illumination N-doping always makes the catalyst worse.

    This may be understood by the generally accepted fact that substitution of O-atoms with nitrogen and the following introduction of an N-2p inter-band level leads to increased recombination rates (lower electron-hole lifetime).

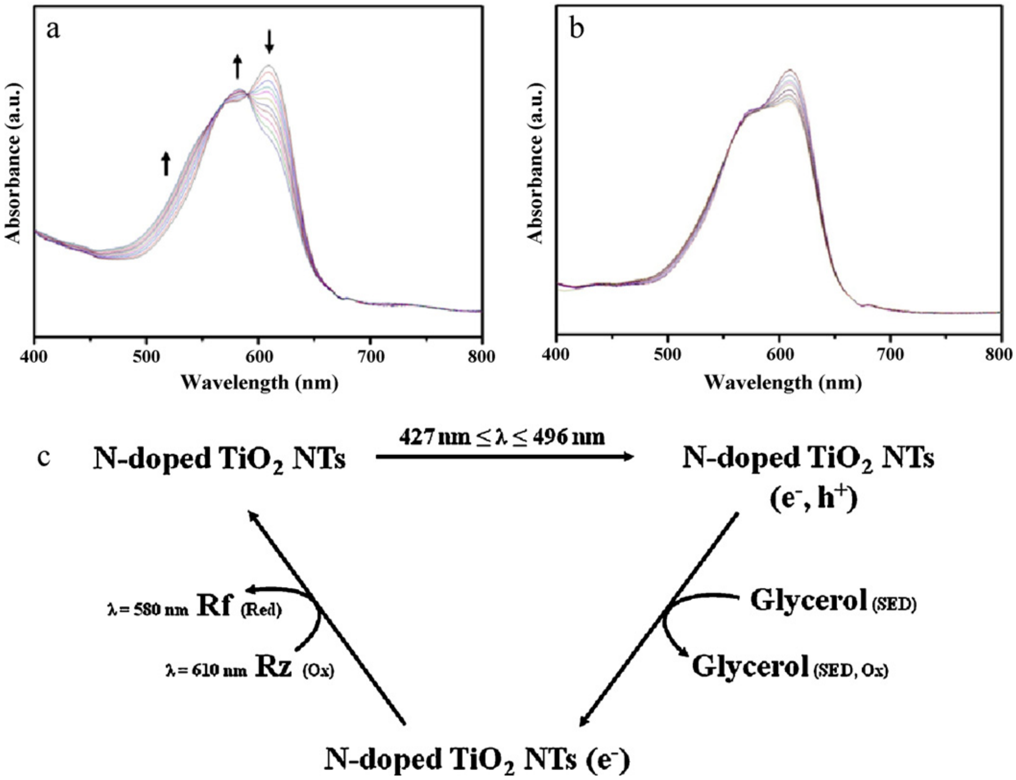

Fig. 3. The visible light photocatalytic activity as a function of measuring time. Redox conversion of Rz dye (a) N-doped TiO_2 NT and (b) pure TiO_2 NT, respectively. (c) Proposed photocatalytic reaction scheme of the indicator ink on a N-doped TiO_2 NT.

Table 1
Quasi-quantitative comparison of photocatalytic oxidation activity for undoped and N-doped anatase TiO_2 nanotubes. Activity (evidenced by the CO_2 signal) is tested under both UV, 367 nm, and violet light, 406 nm, under roughly similar photon fluxes of about 1.4×10^{19} photons/cm^2 s. The probe reactions are the oxidation of CO to CO_2 (measured in a mix of 2:1 CO:O_2 mixture at 1 bar total pressure) and oxidation of methane to CO_2 and H_2O (measured in a mix of 2% CH_4 in air at 1 bar total pressure).

	Normalized CO_2 production rate			
	CO oxidation		CH_4 oxidation	
	Undoped nanotubes	N-doped nanotubes	Undoped nanotubes	N-doped nanotubes
UV (367 nm, 79 mW/cm^2)	100	3.3(1)	3.0(3)	0.43
VIS (406 nm, 65 mW/cm^2)	0.24	0.12	<0.01	0.04

(2) N-doping has a clear beneficial effect under visible-light illumination in the dye test.

In the dye test the photo-electrons in the conduction band drive the facile, single electro reduction of resazurin to resorufin. Since this reaction is kinetically very fast the N-doped material suffers little penalty from its shorter electron–hole lifetime. At the same time, the undoped material is severely limited by low absorption of visible-light.

(3) Both N-doped samples and undoped samples have very little activity under visible-light for photo-mineralization.

Under photocatalytic mineralization conditions the photo-electrons in the conduction band are driving the reduction of O_2 which is a four-electron reaction and is known for its sluggish kinetics and high overpotential. Therefore the photo-electrons are much more likely to recombine with holes in the inter-band N-2p state instead of reducing O_2 causing the N-doped material to perform poorly. Of course, the undoped material is still limited by low absorption in this case and thus neither material works.

To summarize, we have an example of a catalyst that hardly works under visible light (for photo-oxidation reactions in general) despite the positive dye-test result. This underscores the need to interpret dye-test results with great caution [25]. To confirm photocatalytic activity it seems necessary to test at least one photo-oxidation reaction where the oxidant is O_2. Probe reactions often encountered in the literature include photo-oxidation of compounds such as CO, CH_4, methanol, acetaldehyde, stearic acid or even halogenated compounds such as pentachlorphenol.

4. Conclusions

Nitrogen-doped vertically aligned transparent TiO_2 nanotube coated windows were successfully prepared and the activity for the reduction of resazurin dye was observed—even under visible light irradiation. However, those same samples showed much reduced UV activity and almost no visible light activity for photocatalytic CO-oxidation and methane oxidation when compared with undoped TiO_2 nanotube coated windows. It seems, there is no technologically relevant light source (including sunlight) where N-doping is of any benefit for self-cleaning activity of TiO_2 nanotubes insofar as the oxidation of methane, and perhaps CO, is a relevant model-reaction. This result demonstrates the need to always confirm photocatalytic activity using O_2 as the oxidant rather than only relying on a dye test.

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