Journal of Photochemistry and Photobiology A: Chemistry 216 (2010) 156–166

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

The combinatorial atmospheric pressure chemical vapour deposition (cAPCVD) of a gradating substitutional/interstitial N-doped anatase TiO_2 thin-film; UVA and visible light photocatalytic activities

Andreas Kafizas, Colin Crick, Ivan P. Parkin*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

ARTICLE INFO

Article history:
Available online 6 July 2010

Keywords:
Nitrogen doping
Interstitial
Substitutional
Photocatalysis
Thin-film
Anatase

ABSTRACT

Combinatorial atmospheric pressure chemical vapour deposition (cAPCVD) was used to synthesise a film with gradating substitutional (N_s) and interstitial (N_i) nitrogen dopant concentrations across an anatase TiO_2 thin-film. A transition from predominantly N_s-doped, to N_s/N_i mixtures, to purely N_i-doped titania was observed by X-ray photoelectron spectroscopy (XPS) analysis of positions across the film. We believe this to be the first time that such a gradient from N_i to N_s-doping has been achieved by a CVD process in a single film. The film was characterized by X-ray diffraction, Raman, and atomic force microscopy. Film thicknesses and bandgap energies were calculated from Swanepoel and Tauc plot manipulations of transmittance spectra. The photocatalytic activity to UVA ($365\,nm = 1.75\,mW\,cm^{-2}$) light was assessed by monitoring colour changes in digital images of an even layer of intelligent ink deposited by an aerosol-spray method and by UV–visible spectroscopic assessment of the degradation of an aqueous methylene blue dye. The photo-activity to visible light (indoor white light source) was assessed by monitoring the degradation of a stearic acid over-layer. This allowed for the systematic investigation on the effect of N_s and/or N_i-doping in anatase TiO_2 and the dopant concentration on the thin-film's photocatalytic activity. The results indicated that N_s-doping of anatase titania causes detriment to the film's photocatalytic activity to UVA-light. It was also found that purely N_i-doped anatase made a marginally more active visible light photocatalyst than predominantly N_s-doping. The differences were related to increased recombination effects in N_s-doped systems versus N_i-doped systems. Films synthesized by the cAPCVD route analysed in conjunction with mapping analysis tools provide a shortcut to identifying numerous phases and compositions and their functional property relationships on a single film, offering a rapid method for analysis of phase-space.

1. Introduction

Anatase titanium dioxide (TiO_2) is the leading material for semiconductor photocatalyst applications due to its biological and chemical inertness, mechanical robustness durability to multiple photocatalytic cycles, relatively low cost and high photo-activity [1,2]. Anatase titania has been used for the degradation of organic pollutants, bacteria, cancer cells and viruses on nano-crystalline powders or thin-films [3–14]. The photo-degradation of the organic material occurs at the semiconductor's surface when photons greater than or equal to the bandgap energy is provided in the presence of oxygen. The bandgap energy of anatase titania (3.2 eV) requires photons that fall in the UVA portion of the electromagnetic spectrum or of higher energy (typically $\lambda \leq 388\,nm$) to cause the photo-excitation of an electron from the valence to the conduction band and creation of an electron–hole pair. An energy stabilising migration of these holes (h^+) and electrons (e^-) predominantly formed within the bulk of the semiconductor to the surface of the film occurs. If recombination of the electron–hole pair does not occur, surface electrons reduce species such as atmospheric O_2 to superoxide O_2^-, which can be further reduced to H_2O and holes oxidise surface-bound hydroxyl groups into highly reactive hydroxyl radical species. The surface radicals/reduced species formed subsequently oxidise the surface-bound organic pollutant into mineral acids and CO_2.

A further consequence of photo-excitation of anatase titania is photo-induced superhydrophilicity (PSH), which has been shown to proceed by an alternative mechanism to photocatalysis, with the surface becoming more wettable due to hydroxyl formation. It is the combination of PSH and photocatalytic properties that have made anatase titania so highly suitable for self-cleaning thin-film coatings on glass [15] and tiles [16]; where the hydrophilic properties allow for greater surface-wetting and washing and the photocatalysis promotes degradation of organic residues. Although a range of

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* Corresponding author. Tel.: +44 020 7679 4669; fax: +44 020 7679 7463.
E-mail address: i.p.parkin@ucl.ac.uk (I.P. Parkin).

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doi:10.1016/j.jphotochem.2010.06.034

products extending the use of anatase titania in water and air purification systems, sanitary-ware and deodorizing products have been commercially introduced [17], their use is limited to environments where sufficient UV-light is available for them to function. Although the more thermodynamically stable rutile form of titania [18] has a lower associated bandgap energy (3.0 eV); commercial applications of TiO_2 have predominantly featured the anatase phase. It has been a matter of considerable debate as to whether phase pure anatase, rutile or synergistic anatase–rutile mixtures provide a more effective photocatalyst [1]; however recent studies encompassing a range of pure/mixtures of anatase/rutile indicated phase pure anatase gave more photocatalytically active thin-films [19].

As a more significant portion of light is contained in the visible part of the solar spectrum, compared with UV-light, it has thus become an important goal to develop more red-shifted titania materials to enhance their photo-activity. As such, there have been a large number of studies aimed at modifying TiO_2 *via* doping or composite formation [20–27]. The inclusion of specific dopants alter the band structure of TiO_2 and can push the bandgap to more visible wavelengths; composites can also induce charge stability and transport of photo-excited electron–hole pairs within the material and increase the quantum efficiency.

Many research groups have found that N-doping of titania leads to greater visible light photo-activity [28–33]; however there is division on how this is achieved [2]. As the N dopant can enter the TiO_2 matrix by either direct substitution of an oxygen site (N_s) or by stationing itself interstitially (N_i) there is uncertainty in the literature as to which type of nitrogen insertion yields the more active visible light photocatalyst. Electron paramagnetic resonance (EPR) can be used to determine the nature of the N-dopant insertion in anatase titania powders [32,33]. X-ray photoelectron spectroscopy (XPS) has been shown to differentiate between N_i and N_s sites with N1s peaks at 400 eV and 396 eV respectively [34–36]. In contrast, some researchers suggest that oxygen vacancy (V_O) formation is fundamental to the visible light photocatalytic enhancement. In that scenario, the substitutional incorporation of nitrogen into anatase titania encourages V_O formation [37].

Theoretical DFT studies have modelled the effect on the density of states within anatase titania when N-doped with either N_s or N_i; with contrasting differences [38–40]. Calculations showed that N_s substitution causes the valence band to increase by 0.14 eV due to the overlap between nitrogen and oxygen 2p orbitals whereas N_i-doping creates an inter-band state 0.74 eV above the valence band [38,39]. The propensity to form oxygen vacancies in N-doped titania were shown to increase compared with an un-doped system. From calculations it was shown that the energy of V_O formation decreased from 4.2 eV in un-doped to 0.6 eV in N-doped anatase. In the case of N_s-doping, it is clear that the associated bandgap narrowing could induce a more active visible light photocatalyst in a single-electron excitation process. However, a dual-electron excitation process for N_i was suggested by Peng et al. [41]; with electrons initially photo-excited to the inter-band state and subsequently to the conduction band. Although it has been suggested that oxygen vacancies would encourage recombination, calculations by Zhao et al. indicated that V_O formation would create vacancies 1 eV below the conduction band and act as active traps that encourage photocatalysis [40]. Even though there is no consensus to the mechanism by which the visible light photocatalytic enhancement is achieved in N-doped TiO_2, there is agreement that a saturation point in N-doping occurs with a trade off between a narrowing of the bandgap and an increase in the detrimental effects of electron–hole recombination processes [29].

Chemical vapour deposition (CVD) is a technique that has been used to produce anatase titania thin-films of typically superior adhesion, durability and uniformity than the corresponding physical vapour deposition (PVD) counterpart [42–46]. However, single films with significant variations in thickness, phase and composition have been achieved using combinatorial atmospheric pressure chemical vapour deposition (cAPCVD) [47–52,19]. The investigation of such films, using high-throughput mapping analysis techniques [52–55], allowed for rapid determination of functional property relationships. For example, the effect of increased oxygen content within a vanadium oxynitride thin-film on the conductivity and reflectance properties [47]. However, cAPCVD was recently used to synthesise a N-doped thin-film with gradating N_s content and phase (anatase–rutile content) [48]. Photocatalytic activity mapping [53,54] of the film demonstrated the effect of N_s upon the films photo-activity to UVA 365 nm light in addition to the role of an increased rutile phase component. The nitrogen dopant was introduced into the TiO_2 matrix using ammonia gas as the source; analogous to previous work performed by Yates et al. [55]. In correlation with their APCVD produced N_s-doped thin-films, a decrease in the photocatalytic activity to UVA-light was also observed. APCVD deposited N_s-doped anatase TiO_2 thin-films were also produced by Duminica et al. using hydrazine as the nitrogen source. Films again showed lower photocatalytic activity to UVA-irradiation; however increased visible light activity was noted [56]. Contrastingly, using a t-butylamine nitrogen source, Dunnill et al. were able to synthesise purely N_i-doped anatase thin-films by APCVD [34–36]. Although these films were not tested to UVA-light, a marked increase in the visible light photocatalytic activity in the destruction of a stearic acid over-layer was observed.

From the literature, it is clear that the use of ammonia gas as a nitrogen source in APCVD synthesis encourages N_s-doping within anatase thin-films [48,49]; with higher ammonia concentrations encouraging the formation of a new phase, pseudo-brookite Ti_3O_4N, which is itself an active photocatalyst [50,51,19]. Although predominantly N_i insertion of anatase was observed when t-butylamine was used, it was suggested that the reaction proceeded through a thermal decomposition step to ammonia gas before surface-reaction and insertion [34–36]. It was therefore intuitive that a more heavily diluted concentration of ammonia gas during depositions may encourage N_i-doping.

In this paper we describe the combinatorial atmospheric pressure chemical vapour deposition (cAPCVD) synthesis of an anatase TiO_2 thin-film with gradating nitrogen dopant from predominantly N_s-doping to purely N_i-doping using a triple source of precursors: $TiCl_4$ [metal source], ethyl-acetate [oxygen source], and ammonia gas [nitrogen source]. The ammonia source was diluted with a plain flow of N_2 that enabled a significantly lower ammonia concentration during the deposition compared to a previous study [48]. This encouraged the formation of a N_s to N_i-doping gradient across the thin-film. Correlations of the effect of N_s and/or N_i-doping of anatase TiO_2 on the thin-film's physical properties and photocatalytic activities to UVA and visible light were assessed. This work also illustrates how the combinatorial APCVD approach can be used to rapidly analyse phase-space and how it can be used to identify optimum material properties.

2. Materials and methods

All chemicals used in this study were purchased from Sigma–Aldrich Chemical Co; resazurin 92%, hydroxyl ethyl cellulose (HEC) [average $M_v \approx 90{,}000$], glycerol 99.5%, isopropanol 99.98%, acetone 99%, ethyl-acetate 99%, and titanium (IV) chloride 99.9%. Nitrogen and ammonia (oxygen free) gas cylinders were supplied by BOC. The glass substrate, consisting of a standard piece of 3.2 mm thick float glass coated with a 50 nm SiO_2 barrier layer that inhibited ion diffusion from the glass, was supplied by the Pilkington NSG Group.