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Nitrogen-modified nano-titania: True phase composition, microstructure and visible-light induced photocatalytic NO_x abatement

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ABSTRACT

Titanium dioxide (TiO_2) is a popular photocatalyst used for many environmental and anti-pollution applications, but it normally operates under UV light, exploiting ~5% of the solar spectrum. Nitrification of titania to form N-doped TiO_2 has been explored as a way to increase its photocatalytic activity under visible light, and anionic doping is a promising method to enable TiO_2 to harvest visible-light by changing its photo-absorption properties. In this paper, we explore the insertion of nitrogen into the TiO_2 lattice using our green sol–gel nanosynthesis method, used to create 10 nm TiO_2 NPs. Two parallel routes were studied to produce nitrogen-modified TiO_2 nanoparticles (NPs), using HNO_3+NH_3 (acid-precipitated base-peptised) and NH_4OH (totally base catalysed) as nitrogen sources. These NPs were thermally treated between 450 and 800 °C. Their true phase composition (crystalline and amorphous phases), as well as their micro-/nanostructure (crystalline domain shape, size and size distribution, edge and screw dislocation density) was fully characterised through advanced X-ray methods (Rietveld-reference intensity ratio, RIR, and whole powder pattern modelling, WPPM). As pollutants, nitrogen oxides (NO_x) are of particular concern for human health, so the photocatalytic activity of the NPs was assessed by monitoring NO_x abatement, using both solar and white-light (indoor artificial lighting), simulating outdoor and indoor environments, respectively. Results showed that the onset of the anatase-to-rutile phase transformation (ART) occurred at temperatures above 450 °C, and NPs heated to 450 °C possessed excellent photocatalytic activity (PCA) under visible white-light (indoor artificial lighting), with a PCA double than that of the standard P25 TiO_2 NPs. However, higher thermal treatment temperatures were found to be detrimental for visible-light photocatalytic activity, due to the effects of four simultaneous occurrences: (i) loss of OH groups and water adsorbed on the photocatalyst surface; (ii) growth of crystalline domain sizes with decrease in specific surface area; (iii) onset and progress of the ART; (iv) the increasing instability of the nitrogen in the titania lattice.

1. Introduction

Major 21st century concerns are ever-increasing environmental pollution, sustainability and emerging antibiotic-resistant bacteria [1,2]. It has been demonstrated that indoor and outdoor air pollution is associated with significant adverse effects on public health [3–5], with particulate matter (PM), nitrogen dioxide (NO_2) and ozone (O_3) being of particular concern [6]. Recent studies have shown significant variations in, and high levels of, outdoor air pollution on a small or local scale within urban areas for pollutants such as nitrogen oxides (NO_x=NO and NO_2), with long-term average exposure having serious repercussions on health [7–9]. Semiconductor photocatalysis is one of the most promising green technologies to combat this problem [10–12]. It represents an easy and viable way to take free advantage of the primary source of energy available on earth: solar light. This enables a sustainable, environmentally friendly solution for most forms of indoor and outdoor atmospheric pollution [13–15].

Titanium dioxide (titania, TiO_2) nanomaterials are the most extensively used and investigated semiconductor materials for photocatalytic applications [16]. TiO_2 is chemically stable, environmentally compatible, cost-effective, the photocatalytic reaction takes place at mild operating conditions with no need for other chemical additives, and many recalcitrant and persistent

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pollutants can be degraded [17–20]. Although TiO_2 crystallises in at least 11 bulk and/or nanocrystalline phases [21], anatase, rutile and brookite are the most used for photocatalytic applications. Anatase TiO_2 is a wide band gap (E_g) semiconductor, the photocatalytic reaction exploits UVA–light (315–390 nm), which makes up only 3–5% of the total solar energy spectrum [22]. Rutile has a slightly smaller band gap, and is active just on the edge of the visible range, at around 400 nm. Therefore, the vast majority of the available solar energy is "wasted" in such materials, and we need to exploit the visible region (390–780 nm), which contains 44–47% of solar energy. To override this weakness, and move E_g into the visible region, the electronic structure of TiO_2 has been modified using various, usually metallic (cationic), dopants [23–25], or has been made in the form of composite photocatalysts [26,27], or heterojunction photocatalysts [28,29]. However, anionic doping would appear to be a simple and viable method to produce visible-light sensitive photocatalysts [30].

TiO_2 nitrification under a nitrogen atmosphere, and its use as a visible-light ($\lambda < 460$ nm) photocatalyst, was first published in the 1970's (*e.g.*, Hirai et al. in 1978) [31]. However, this "forgotten" topic was given a major boost in 2001, when Asahi et al. demonstrated in *Science* that N-doped TiO_2 has greater photocatalytic activity under visible-light exposure [32]. Since then, non-metal doping has been explored as a promising way to harvest visible-light, making TiO_2 a visible-light active photocatalyst, by changing its photo-absorption properties [19,30,33]. The actual mechanism through which nitrogen favours visible-light absorption is controversial: Asahi et al. using local density approximation (LDA) calculations, proposed a band gap narrowing due to a mixing of N *p* states with the O 2*p* states in the titania valence band [32]. By contrast, Di Valentin et al. used density functional theory (DFT) calculations and larger supercell models, to show the formation of N 2*p* states almost totally localised on the N atom, just above the top of O 2*p* band [34–36]. A paper by Lee et al. states that the use of a base during the peptisation process to form a sol could also affect the TiO_2 phases that result [37]. They found that an acid-hydrolysed base-peptised sol was better for preserving the anatase phase at higher temperatures, giving a pure anatase product even at 700 °C. On the other hand, a base catalysed hydrolysis followed by acid peptisation was better for creating slightly smaller nanoparticles, but this had begun to convert to rutile at only 500 °C.

We have developed a novel aqueous green nanosynthesis route to create 10 nm anatase NPs, which has been reported previously [38,39]. Therefore, we decided to explore the insertion of nitrogen into the TiO_2 lattice using our green sol–gel nanosynthesis method, and that two parallel routes would be studied, using a totally base catalysed process, and an acid-precipitated base-peptised one. To this end, we synthesised nitrogen modified TiO_2, using HNO_3+NH_3 (acid-precipitated base-peptised) and NH_4OH (totally base catalysed) as nitrogen sources. Dried gels were thermally treated at four different temperatures (450, 600, 700 and 800 °C), and the actual amount of both amorphous and crystalline phases was determined by X-ray powder diffraction (XRPD) data *via* the Rietveld–RIR method. The microstructure of the prepared samples was fully characterised with an advanced XRPD method, whole powder pattern modelling (WPPM). The optical properties of the nitrogen-modified TiO_2 were analysed by diffuse reflectance spectroscopy (DRS). The functional property defined by assessing the photocatalytic activity (PCA) of the nitrogen-modified TiO_2 photocatalyst in the gas–solid phase, monitoring nitrogen oxides ($NO+NO_2=NO_x$) abatement. Solar and white-light (indoor artificial light) lamps were used, in order to simulate outdoor and indoor environments, respectively.

2. Experimental

2.1. Sample preparation

The synthesis method was based on the aqueous sol–gel green nanosynthesis method developed by the authors, and reported previously [38,39]. The hydrolysis of titanium(IV)isopropoxide (Ti-*i*-pr, Aldrich, 97%) was achieved by the controlled, dropwise addition of a small excess of distilled water (5:1 water:Ti-*i*-pr), diluted to 20% water in a solution of isopropylalcohol (IPA, propan-2-ol). The Ti-*i*-pr was also diluted to a 20% solution in IPA. This Ti-*i*-pr solution was hydrolysed by the dropwise addition of the water/IPA solution, while being stirred mechanically at 800–1200 RPM at room temperature, the entire addition taking approximately 30 min.

For the acid-precipitated base-peptised process (NO_3+NH_3), concentrated HNO_3 (Aldrich, 65%) was added in a ratio of Ti^{4+}: HNO_3 of 5:1 to the water–IPA solution, and this was all added dropwise to the Ti-*i*-pr solution, as in our standard sol–gel preparation of TiO_2. There was no immediate precipitation as the water was added, with a white, cloudy, gelatinous suspension forming by the end. The precipitated mixture was evaporated to a white jelly-like mass on a rotary evaporator at 60 °C and 140 mPa. However, at this stage, NH_3 (Aldrich, 25% solution) was added in enough water to restore the mixture to the original volume, with a ratio of Ti:NH_3 of 2.5:1 (double the proportion of acid). The suspension was dispersed, and then the water removed on the rotary evaporator at 65 mPa and 60 °C, drying to an orange powder, with no smell of organics or ammonia. When water was added again to a concentration of 1 M Ti^{4+}, the mixture remained as a fine milky suspension, and no true sol was formed–the NH_3 did not peptise the precipitate to make a stable sol. Upon subsequent drying, it formed a very fine, off-white powder.

For the totally base catalysed synthesis (referred to as NH_4OH, to differentiate it from the acid process above), the Ti-*i*pr solution was precipitated without the addition of any acid to the water–IPA solution. This resulted in an instantaneous formation of a milky precipitate, but without any subsequent gelling with further addition, resulting in a coarse suspension at the end. The solution was evaporated to dryness as above forming a white powder. As above, NH_3 was added, in a ratio of Ti:NH_3 of 2.5:1, in sufficient water to restore the mixture to its original volume, and the powder dispersed. The water was removed as above, and again a fine white powder formed, with no sign of gelling. When dispersed once more in water, this remained a fine milky suspension, and did not form a stable sol. It dried to a fine, white powder.

Both powders were then further dried overnight at 75 °C in a drying oven. Both dried powders were thermally treated at four different temperatures (450, 600, 700 and 800 °C) under a static air flow, using a muffle furnace. The heating/cooling rate was 5 °C min^{-1}, with a 2 h dwell time at the selected temperature. Samples were referred to as **TiA** (with NH_4OH, base catalysed only, **A**=ammonia), and **TiNAA** (with HNO_3 and NH_3, acid hydrolysed and based peptised, **NAA**=nitric acid & ammonia). A number representing the maximum temperature reached was added to the chosen abbreviation (*i.e.* **TiA450** standing for sample **TiA** thermally treated at 450 °C).

2.2. Sample characterisation

2.2.1. X-ray powder diffraction (XRPD)

Quantitative phase analysis (QPA), *i.e.* the determination of the actual amount of both crystalline and amorphous phases present in the prepared samples, was accomplished *via* XRPD with the combined Rietveld–RIR method [40]. XPRD data were collected using a θ/θ diffractometer (PANalytical X'Pert Pro, NL) equipped