



# Photocatalytic Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> nanoparticles for glazed ceramic tiles

Andre L. da Silva<sup>a,b</sup>, Dereck N.F. Muche<sup>b</sup>, Sanchita Dey<sup>b</sup>, Dachamir Hotza<sup>a</sup>, Ricardo H.R. Castro<sup>b,\*</sup>

<sup>a</sup>Department of Chemical Engineering (EQA), Graduate Program on Materials Science and Engineering (PGMAT), Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis, SC, Brazil

<sup>b</sup>Department of Chemical Engineering and Materials Science & NEAT ORU, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA

Received 5 November 2015; received in revised form 2 December 2015; accepted 4 December 2015

## Abstract

TiO<sub>2</sub> nanoparticles are currently used as coating for self-cleaning building products. In order to achieve high self-cleaning efficiency for outdoor applications, it is important that titania is present as anatase phase. Moreover, it is desirable that the particle sizes are in nano-range, so that a large enough surface area is available for enhanced catalytic performance. In this work, TiO<sub>2</sub> nanoparticles doped with 0–5 mol% Nb<sub>2</sub>O<sub>5</sub> were synthesized by co-precipitation. Nb<sub>2</sub>O<sub>5</sub> postponed the anatase to rutile transformation of TiO<sub>2</sub> by about 200 °C, such that after calcination at 700 °C, no rutile was detected for 5 mol% Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub>, while undoped TiO<sub>2</sub> presented 90 wt% of the rutile phase. A systematic decreasing on crystallite size and increasing on specific surface area of TiO<sub>2</sub> were observed with higher concentration of Nb<sub>2</sub>O<sub>5</sub> dopant. Photocatalytic activity of anatase polymorph was measured by the decomposition rate of methylene blue under ultraviolet and daylight illumination and compared to commercial standard catalyst (P25). The results showed enhanced catalysis under UV and visible light for Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> as compared to pure TiO<sub>2</sub>. In addition, 5 mol% Nb<sub>2</sub>O<sub>5</sub>-doped TiO<sub>2</sub> presented higher photocatalytic activity than P25 under visible light. The enhanced performance was attributed to surface chemistry change associated with a slight shift in the band gap.

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**Keywords:** Titanium dioxide; Rutile; Anatase; Photocatalysis; Ceramic tiles

## 1. Introduction

Oxide photocatalysts have been intensively investigated for applications in air and water remediation, self-cleaning and self-sterilizing surfaces. Among different photocatalytic materials, titanium dioxide (TiO<sub>2</sub>) is by far the most attractive choice due to its high chemical stability, environmental inertness, and relative low cost [1–3]. One of the most emergent applications of TiO<sub>2</sub> is on glazed ceramic tiles [4–6]. The most common deposition techniques of TiO<sub>2</sub> on tile surfaces are roller printing [4], ink jet printing [4], spraying [5–7] and dip coating [8]. Ceramic tiles have received particular attention in the last years regarding innovative applications and manufacturing processes, such as reduced thickness products [9,10], digital decoration

[11] and antimicrobial activity [12,13], which aggregate value to those building materials.

When a TiO<sub>2</sub> photocatalyst site absorbs a photon with energy equal to or greater than its band-gap, an electron–hole pair is generated; subsequently, the pair is split into a free electron and a free hole [1]. The photogenerated electron/hole pair promotes the reduction and oxidation of species adsorbed at the surface of the semiconductor and induces oxidative degradation of species in solution through radical reactions [14]. Therefore, when TiO<sub>2</sub> is irradiated with UV-light, it can decompose organic dyes such as methylene blue (MB) [15,16], alizarin S [17,18], crocein orange G [17], methyl red [17,19], and congo red [17,20]. MB is commercially employed in textile, leather and paper industries, and it is one of the most used dyes for measurement of photocatalytic activity. Since dye-containing wastewater can block both sunlight penetration and oxygen dissolution, which are essential for aquatic life, there is considerable interest in treating these colored effluents

\*Corresponding author. Tel.: +1 530 752 3724.

E-mail address: [rhrcaastro@ucdavis.edu](mailto:rhrcaastro@ucdavis.edu) (R.H.R. Castro).

before discharging them to water bodies [21]. Furthermore, discoloration of MB dye as a model pollutant is most often used for testing of materials with self-cleaning properties [5,6,22].

The optimization of TiO<sub>2</sub> performance as photocatalyst is an active research field given the above mentioned industrial relevance. This entails understanding the dependences of the catalytic behavior on the system chemistry, structure and microstructure. TiO<sub>2</sub> has three main polymorphs: rutile, anatase and brookite. Among those, anatase presents generally the highest activity, which is improved from high crystallinity and surface area [23–25], although a mix of anatase and rutile can improve photoactivity in some cases [26–29]. Kordoult et al. [30] have studied the photodegradation of two representative azo-dyes, one acidic (Orange G) and one basic (Yellow 28) for different anatase-rutile ratios. For both azo-dyes they have showed that the increasing of rutile percentage decreases the photoactivity ratio.

Several dopants have been used to postpone the anatase-to-rutile transformation (ART) while simultaneously changing physical-chemistry of the surface of TiO<sub>2</sub> in order to increase its photocatalytic performance. For instance, rare-earth-doped TiO<sub>2</sub> has led to increased photocatalytic activity under visible light as compared to pure titanium dioxide [31–33]. Transition metals have also improved activity by reducing the recombination of photogenerated electrons and holes [34–36]. Non-metal doped TiO<sub>2</sub> has shown improvement on absorption and photocatalytic activity in the visible light region [37,38].

Niobium has been considered a promising candidate for enhanced catalysis of titania [39]. The ionic radius of Nb<sup>5+</sup> (0.64 Å) is only slightly larger than Ti<sup>4+</sup> (0.605 Å). Thus, Nb<sup>5+</sup> can form solid solution in the lattice of TiO<sub>2</sub>. To compensate the excess charge of Nb<sup>5+</sup> in substitution to Ti<sup>4+</sup>, one Ti cation vacancy may be created per 4 Nb introduced. Alternatively, the stoichiometric reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup> may also occur depending on preparation conditions, which will introduce shallow donor levels below the conduction band (CB) edge of TiO<sub>2</sub> [40,41]. The electronic transition from valence band (VB) to these donor levels will be excited by the visible light and therefore render the Nb-doped TiO<sub>2</sub> photocatalyst to be visible light responsive, such as nonstoichiometric TiO<sub>2</sub> [42].

Nb<sub>2</sub>O<sub>5</sub>-doped titania has been shown to have higher photocatalytic activity for the degradation of diquat dibromide monohydrate under UV-light as compared to pure TiO<sub>2</sub> [43]. Photocatalytic oxidation of 4-chlorophenol and iodide as well as the photoreduction of hexavalent chromate (Cr<sup>6+</sup>) have been studied by Nb-TiO<sub>2</sub> catalysts, which presented enhanced photocatalysis under visible light [44].

In this work, the temperature of the anatase to rutile phase transition as a function of Nb<sub>2</sub>O<sub>5</sub>-doping concentration was studied in titania nanoparticles prepared by coprecipitation in order to enhance anatase stability. The presence of anatase or anatase/rutile mixed phases at the 700–800 °C would allow the use of titania powder as a coating in glazed ceramic tiles, particularly for those processes which include a second firing stage at this temperature range for decoration purposes.

## 2. Experimental procedure

### 2.1. Sample preparation

TiO<sub>2</sub> nanoparticles containing 0, 0.5, 1, 2, and 5 mol% Nb<sub>2</sub>O<sub>5</sub> were synthesized by co-precipitation. The respective compositions were named 0NbTi, 0.5NbTi, 1NbTi, 2NbTi and 5NbTi. Titanium (IV) isopropoxide (TTIP, Sigma-Aldrich, ≥ 97%) and niobium butoxide (NB, Sigma-Aldrich, 99%) were used as Ti and Nb precursors, respectively. TTIP and NB were mixed for 10 min and they have visually formed a homogeneous solution. No partially pre-hydrolyzed was observed in this step. Thus, the solution was added dropwise into an ammonium hydroxide solution (NH<sub>4</sub>OH, 5 M, Fisher Scientific) under vigorous stirring. The colloidal suspension was centrifuged at 3000 rpm for 5 min to separate the nanopowder from the liquid. The powder was then washed three times (in water, water/ethanol 1:1 in volume, and ethanol, respectively). The samples were dried at 90 °C for 72 h and ground with a pestle and mortar. The calcination procedure was performed in a box furnace (Lindberg/Blue M) at different times and temperatures (450–900 °C). For the photocatalytic experiments, calcination temperatures that lead to anatase-only with maximum specific surface area were selected for each composition, i.e. 450 °C for 0NbTi, 2NbTi and 5NbTi; and 500 °C for 0.5NbTi and 1NbTi.

### 2.2. Characterization of powders

Powder X-ray Diffraction (XRD) patterns were obtained using a Bruker AXD D8 Advance diffractometer (Bruker AXS, Madison, WI) with CuK $\alpha$  radiation, and  $\lambda = 1.5406$  Å, operated at 40 kV and 40 mA. Data were collected in the range 20–90° (2-theta) and the pattern profile fitting was performed using the Jade 6.1 (MDI) software to determine crystal structure, phase purity, and crystallite size. Specific surface area measurements were carried out using the Brunauer, Emmett, and Teller (BET) method with nitrogen gas adsorption (Micromeritics Gemini VII). Thermogravimetry results have showed that significant mass changes can only be observed up to 400 °C; hence, this temperature was selected for degassing prior to BET experiment (Micromeritics VacPrep 061, sample degassing system). Surface morphology and particle size distribution were analyzed by High Resolution Transmission Electron Microscopy (HRTEM; Jeol JEM 2500SE with 200 keV). The absorption studies were carried out by UV-visible spectrophotometer (Evolution 220, Thermo Scientific). The UV-vis absorption spectra were recorded in the wavelength range 300–800 nm. The values of the energy band gap were determined applying Kubelka-Munk phenomenological theory assuming the indirect band gap [45].

### 2.3. Photocatalytic activity

The photocatalytic activity of the prepared nanoparticles was assessed in liquid–solid media monitoring the degradation of the organic dye methylene blue (MB, Sigma-Aldrich) under

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