



Continuous flow photocatalytic oxidation of nitrogen oxides over anodized nanotubular titania films

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ABSTRACT

Self ordered nanotubular TiO₂ films of variable morphological characteristics were grown by electrochemical anodization in ethylene glycol based electrolytes. The films were incorporated in a continuous flow reactor and were evaluated for the UV photocatalytic oxidation of nitrogen oxide (NO) gas by varying the flow rate and the pollutant concentration in the 200–1000 ppbv range. After a strong initial response, the photooxidation rate decreased and reached an equilibrium state. Strong dependence of the overall NO concentration on the morphological film parameters was observed which is related to the interplay of porosity and extended surface area. Saturation of the photocatalytic performance was evidenced for nanotubular films with thickness above 14 μm, pointing out the limitations imposed by the UV light penetration depth and the diffusion of the gas pollutants and intermediates into the nanotube channels. Nitrates–nitrites were identified as the principle NO_x photooxidation products.

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1. Introduction

Heterogeneous photocatalysis by nanostructured semiconductors is a well established 'green' nano-technology-based advance oxidation process (AOP) for the destruction of environmental air pollutants [1–5]. Among the different catalysts used for this purpose, titanium dioxide (TiO₂) has been established as the material of choice due to its high photocatalytic efficiency combined with the advantages of chemical stability, low cost and toxicity as well as abundance in nature [1]. TiO₂ has been intensively investigated for the decontamination, deodorization, disinfection and decomposition of various air pollutants, a major category being the nitrogen oxides (NO_x) exhausted from automobiles and industries, which have become a serious source of air pollution in urban areas [2,3]. The photocatalysts are generally immobilized in the form of films on different substrates (e.g. glass, metal). In such a scheme, the pollutant molecules adsorbed on the photocatalyst surface can be efficiently decomposed in real time solar applications, where the light flux (UV part) is of the order of several hundreds μW/cm² [1,6]. Furthermore, immobilized photocatalysts avoid separation–filtration steps and obtain enhanced self cleaning

function due to the combined action of photocatalysis with UV light induced superhydrophilicity [6–8].

Nanoparticle size and phase composition as well as thickness, roughness, morphology, 'real' surface area and porosity are the main factors that influence the photocatalytic efficiency of TiO₂ films. A significant drawback in the overall photocatalytic yield arises from the agglomeration of the TiO₂ nanoparticles and the limited diffusion of pollutant molecules inside the photocatalytic film [9,10]. Optimization of the above parameters according to the target photocatalytic application, has motivated the development of functional, one dimensional TiO₂ nanomaterials: nanotubes, nanorods, and nanowires. Among these promising nanostructures, recent literature mainly focuses on self organized titania nanotubular (NT) arrays grown by electrochemical anodization on titanium foils [8,11–15]. These open nanostructures are highly ordered and present controlled and reproducible morphological characteristics and particular advantages that match the main requirements of efficient photocatalysts including extended surface area, facile diffusion of the pollutant molecules inside the pores, vectorial electron transport along the tubes and low carriers recombination, due to decrease of the lattice defects.

Despite numerous reports on the photocatalytic properties of highly ordered titania nanotubes for aqueous pollutants [8,9,16–18], there are only a few reports on their application for air purification. These include the photocatalytic decomposition of

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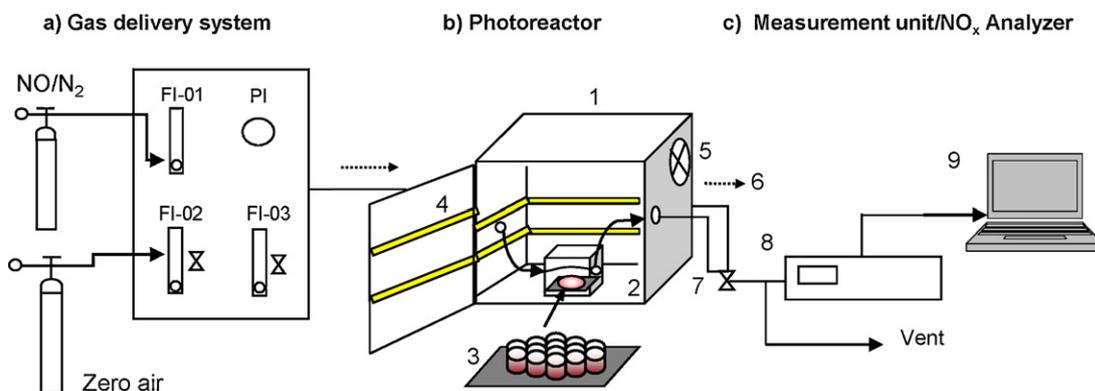


Fig. 1. Schematic presentation of the continuous flow gas environmental reactor used for this study. FI: flow controller/indicator; PI: pressure indicator; 1: irradiation box (0.125 m³); 2: reaction chamber (0.001 m³); 3: TiO₂ NT films (10.7 cm²); 4: UV lamps (10); 5: fans (2); 6: by-pass line; 7: base line; 8: sampling line; 9: data recorder.

volatile organic compounds (VOCs—mainly benzene and toluene) [19,20] and acetaldehyde [21], employing conventional batch type photocatalytic reactors [22]. The above reports [19–21] confirmed the significant influence of the nanotube length on the films photocatalytic activity and have shown that the nanotubes present higher efficiency than the nanoparticles. At the same time the accumulation of intermediate species inside the TiO₂ pores is avoided and the photocatalyst deactivation is inhibited. However, in this current work and for the first time in the literature, according to our knowledge, we have investigated the photocatalytic oxidation of NO pollutants at ppb concentrations and under dynamic experimental conditions corresponding to the real environment, in a continuous flow photocatalytic reactor.

2. Experimental

Nanotubular TiO₂ films were grown by electrochemical anodization of titanium foils (99.6% purity) in ethylene glycol containing NH₄F (0.5 wt.%) by using a conventional three electrode configuration and a high-voltage potentiostat (Jaisle IMP 88). Anodization was carried out under potentiostatic control at 120 V, by pressing the foils against an O-ring in the electrochemical cell, leading to an area of 10.7 cm² exposed to the electrolyte. The film thickness was controlled by varying the anodization time. The prepared films anodized for 1 (NT1), 2 (NT2) and 4 h (NT3), respectively, were amorphous and subsequently they were thermally treated in air at 450 °C, for 1 h, in order to increase their crystallinity.

Surface and cross sectional morphology of the Ti NTs was imaged by scanning electron microscopy (SEM) using a PHILIPS Quanta Inspect (FEI Company) microscope with a tungsten filament operating at 25 kV. Structural characterization was done by Raman spectroscopy employing a Renishaw In-Via spectrometer. Spectra were collected in backscattering configuration, using the 514.5 nm excitation line of an Ar⁺ ion laser. The laser beam was focused on the samples surface using a 50× objective producing a spot of 1.2 μm size. Diffuse reflectance spectra were recorded on a 1200 Hitachi photometer equipped with a 60 mm integrating sphere.

For the photocatalytic experiments, a continuous-flow photocatalytic reactor was used (see Fig. 1), which consists of a reaction chamber, a gas delivery unit and a measurement unit. A compressed gas cylinder of 10 ppmv NO (±2%) balanced in N₂ was used for the creation of NO polluted atmosphere in the photocatalytic reactor (Linde Hellas Ltd.). Prior to its introduction to the photocatalytic chamber, NO was mixed with the appropriate quantity of synthetic air (20.5%, v/v, O₂ and 79.5%, v/v, N₂) adjusting the initial NO concentration to C_{NO} = 200–1000 ppbv. Calibrated flow meters controlled the mixed gas flow rate to either 2–2.5 L/min or 1–1.5 L/min, which are high enough to avoid mass transfer limitations [23,24].

Even though the flow rates were regulated within a ±10% deviation, their records are given with very high accuracy (±2%).

The gas pollutant was introduced into the reactor to a (10 cm × 10 cm × 10 cm) cubic glass cell, containing the catalyst films at the bottom and placed inside a (light) sealed environmental box (Fig. 1). Illumination was provided by ten fluorescent black light blue lamps (15W Philips TLD 15W/08) placed horizontally in pairs on each side of the irradiation box, at a distance of approximately ~20 cm from the photocatalytic material. Total UV irradiance on the photocatalytic films is measured to be 1.4 W/m². The environmental box was further equipped with two fans for keeping the temperature stable and the experiments were performed at ambient pressure (1 atm), room temperature and ≈40% humidity conditions. The concentration of NO_x was measured with a Chemiluminescence NO_x analyzer (Model 42c, Environment S.A.) which was connected in line to the outlet of the reactor. After completing the experiments, the NT films were rinsed with 10 ml water (HPLC gradient grade) and examined for the mineralization residues on the photocatalyst surface via Raman spectroscopy and ion chromatography. Ion analysis was performed in a Dionex ICS-1100 RFIC ion Chromatographer with IonPac AS22 (4 mm × 250 mm) anion-exchange column and an anion self-regenerating suppressor (ASRS 300 4 mm) in auto-suppression mode.

3. Results

3.1. Materials characterization

Electrochemical anodization of Ti in ethylene glycol electrolytes results in the growth of uniform and smooth self-organized NTs with vertical alignment, high porosity and variable morphological characteristics and thickness [11–15]. All these morphological characteristics are controlled by modifying the preparation conditions (anodization time and potential, distance of the electrodes) and the electrolyte composition (type of solvent, porosification agent: HF or NH₄F, and water content). Fig. 2a–f shows scanning electron micrographs (planar and cross sectional views) of the films formed as a function of the anodization time. Additionally, low magnification cross sectional images (Fig. 2g–i), were obtained for estimating the films thickness. As shown in Table 1, increase of the anodization time results in an approximately proportional increase of the film thickness, in agreement with the literature [11–15].

The analysis of the top surface SEM images permits the estimation of several morphological parameters, presented in Table 1. The films grown after 1 h of anodization (NT1) at 120 V show the formation of an organized array of nanotubes with a mean internal diameter (*D*) equal to 60 nm. Increase of the anodization time from 1 to 2 h results in significant increase of *D* to 90 nm. Further increase of the anodization to 4 h imposes minor morphological

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