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Reinforcing blade-cast photocatalytic-titania thin film by titanate nanotubes

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ABSTRACT

Titanate nanotubes/titania gel blends were prepared as composite sol-gel material, deposited on a glass substrate using a doctor blade and calcined in order to create thin films. In order to get an insight in titania nanotubes' ability to reinforce thin films, drying control chemical agents were not used. The effects of titanate nanotubes to titanium n-butoxide ratio on surface morphology, phase composition, mechanical stability and photocatalytic activity were studied. Characterization of the thin films was carried out by means of optical and scanning electron microscopy, powder X-ray diffraction, synchrotron radiation grazing incidence X-ray diffraction and mechanical stability testing. Photocatalytic properties of the obtained thin films were evaluated on the basis of methylene blue degradation. Moderate blends exhibit favourable microstructural features while the dye degradation rate was greater for films with a greater amount of titanate nanotubes.

1. Introduction

Owing to their excellent properties, such as high surface area and excellent photocatalytic activity, as well as simple and affordable hydrothermal preparation process, titanate nanotubes (TNT) are a promising nanoscale-material [1]. When irradiated with UV light, TNT can decompose organic pollutants present on their surface [2]. Therefore, they are intensely investigated as photocatalysts, particularly for waste water treatment. The goal of this process is to mineralize various harmful compounds present in water into harmless compounds such as carbon dioxide and water [3]. However, majority of investigations employ calcination process in order to decompose titanate nanotubes to titania. In such manner, proven powerful photocatalyst is obtained, while original nanotubes morphology is maintained. The fact that investigations of the utilization of titanate nanotubes as photocatalysts are rare, as well as practical and economic considerations favoring a shorter thermal treatment at lower temperatures, are arguments in favor of avoiding the calcination process. In heterogeneous catalytic processes a suspension of TNT material is used. The major drawback of this approach is the need to eventually separate the solid material from the solution [4]. Generally, the separation of the nano-catalyst from the suspension is considered difficult because of nano-dimensions and high colloid stability [5]. In the case of nanotubes, the recovery process is facilitated by the fact that one dimension of the nanotubes is not on the nanometer scale. However, although eased, the separation process is still unavoidable. A practical solution for the avoidance of this shortcoming is the immobilization of nanotubes on a substrate as a thin film [6]. Although the immobilization results in lowering of the surface area and mass transfer limitations [7], it simplifies and cheapens the process and eases its scale-up. The investigations on TNT thin films fabrication on a glass substrate are rare. Notable are papers by Tokudome and Miyauchi [8,9], Suzuki et al. [10] and Ma et al. [11], all of whom used the layer-by-layer method. A far more practical approach to thin film deposition is the doctor blade (tape casting) method. In this process, homogeneous slurry consisting of a suspension of ceramic particles stabilized by additives (binders, dispersants or plasticizers) is placed on a substrate beyond the doctor blade. By moving the blade, the slurry spreads on the substrate to form a thin sheet, which results in a gel-layer upon drying [12]. To the best of our knowledge, the deposition of titanate nanotubes on a glass substrate using a doctor blade has not been previously reported. Also, no data on the needed and appropriate type of TNT-thin-film-stabilizers was available in the literature. However, various compounds were used for the improvement of adherence of titania nanoparticles thin film to the substrate. Among others, titanium alkoxide was utilized for this purpose, titania nanopowder/titania gel composite was prepared, followed by coating of the slurry pastes and thermal annealing [13]. The TNT itself can be considered a thin film stabilizer.

Therefore, in this work we report a simple method of titanate nanotubes deposition on a glass substrate with the aid of titanium n-

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butoxide (TnB). Titanate nanotubes/titania gel blends were prepared via the sol-gel method, deposited on a glass substrate using a doctor blade and finally calcined in order to harden the thin films. The effects of different TNT to TnB ratio on surface morphology, phase composition, mechanical stability and photocatalytic activity using model pollutant degradation were studied in detail.

2. Experimental sections

2.1. Materials and sample preparation

Nanotubes were synthesized by hydrothermal treatment as described by Umek et al. [14] Briefly, 7 g of titania powder (Evonik P25, Evonik Industries, Germany) were added in a 56 cm^3 of 10 M NaOH (Kemika, Croatia) aqueous solution, mixed on a magnetic stirrer for 90 min and sonicated for 15 min. The mixture was then transferred into an autoclave with a 70 cm^3 PTFE container inside. The autoclave was kept in an oven at 135 °C for 72 h. The precipitates were recovered by centrifugation and rinsed in sequence: with distilled water to remove excess NaOH, with 0.1 M HCl (Kemika, Croatia) to enable sodium-to-hydrogen cation exchange and yield hydrogen titanate, and with distilled water and ethanol to remove excess HCl. The resultant nanotubes were then dried at 60 °C for 24 h.

In order to investigate its thermal stability, a part of the TNT sample was thermally treated at 200 and 250 °C for 2 h. Also, in order to investigate thermal evolution of the TnB gel, pure titanium n-butoxide, ($Ti(O^nBu)_4$, 98%, Alfa Aesar, Germany) was hydrolysed by pouring a small quantity of the butoxide into a large Petri dish and exposing it to atmospheric moisture for 72 h. A part of the prepared gel was thermally treated at 200 °C for 2 h.

For the thin films preparation dense pastes were prepared as follows: 1 g of isopropanol was mixed with various amounts (0, 0.2, 0.4, 0.8, 1.6 g) of TnB using a magnetic stirrer. The solutions were stirred for 30 min at room temperature. 0.3 g of titanate nanotubes were grinded for 5 min using agate mortar and pestle to break up macroscopic agglomerates. Then the prepared TnB solution was added into the mortar and blended with titanate nanotubes. After 1 min of intensive homogenization the prepared pastes were tape casted on soda lime glass using the doctor blade method [12]. The glass was previously washed with detergent and rinsed with demineralized water and isopropanol.

For thin film deposition four-face blade film applicator (Qualtech Products Industry, USA) (face with 100 μm gap) was utilized. The blade was positioned near one end of the glass substrate; the sample was put in place in front of the applicator and manually drawn by the blade. The obtained composite thin films were then exposed to air for 72 h in order to complete the process of hydrolysis with atmospheric moisture and condensation and enable complete drying of the sample. Then the samples were heated to 200 °C at 1 °C min^{-1} and kept for 2 h. The samples were denoted NTD0 (0 g of TnB), NTD1 (0.2 g of TnB), NTD2 (0.4 g of TnB), NTD3 (0.8 g of TnB) and NTD4 (1.6 g of TnB).

2.2. Methods of characterization

Light microscopy analyses were performed using DynoLite handheld digital microscope (AM4115T, AnMo Electronics Corporation, Taiwan).

The morphology of titanate nanotubes and thin films was investigated with Tescan Vega 3 scanning electron microscope operating at 30 kV as well as Supra 35LV field emission scanning electron microscope operating at 1 kV. Samples for SEM and FESEM characterization were fixed on a sample holder using double-sided carbon conductive tape and then gold-coated using Quorum SC 7620 sputter coater.

The powder X–ray diffraction (XRD) was accomplished using Shimadzu diffractometer XRD 6000 with CuKα radiation. Data were collected between 5 and 65°2θ, in a step scan mode with steps of 0.02° and counting time of 0.6 s.

The thin films samples were analysed at the powder diffraction beamline (MCX) of the Elettra synchrotron radiation facility (Trieste, Italy), on a Huber 4-axis X-ray diffractometer equipped with a fast scintillator detector in Bragg-Brentano grazing incidence setup (GIXRD) using 2.4 GeV synchrotron radiation delivered using bending magnets, where the incident beam energy was 8 keV, corresponding to CuKα1 radiation. The thin films samples deposited on glass substrates were placed on a flat sample holder and adjusted to position using chi-tilting- and z-axis-height-scans. Patterns were collected in range between 5 and 60°2θ, with steps of 0.02°2θ and collecting time of 0.1 s/step, at ambient temperature. The incidence angles were changed from 0.25 to 3°θ.

The UV–vis spectra of the prepared powder samples were obtained using DRS (Perkin-Elmer Lambda 35) equipped with an integrating sphere. The spectra were recorded at room temperature in the wavelength range of 200–800 nm. $BaSO_4$ was used as a reference. The diffuse reflectance spectra were transformed by performing a Kubelka–Munk transformation of the measured reflectance according to:

$$F(R) = \frac{(1-R)^2}{2R}, \quad (1)$$

where F(R) is proportional to the extinction coefficient (α) and R is the reflectance of the "infinitely thick" layer of the solid [15]. The bandgap energy, Eg, was estimated by plotting modified Kubelka-Munk function, $(F(R)h\nu)^n$ vs. photon energy ($h\nu$), the so–called Tauc's plot, followed by extrapolation of the linear region onto the energy axis. In modified Kubelka–Munk function h is the Planck's constant and ν is frequency, the exponent n is associated with electronic transition in the course of optical absorption process and is theoretically equal to ½ and 2 for indirect and direct allowed transitions, respectively [15].

Adhesion of thin film to the substrate was assessed by Scotch tape test. Tape was applied on the surface and removed at a consistent angle and speed. The changes in the thin-film coverage were evaluated using ImageJ program [16], an open source program for image analysis. The percentage of the area covered by film after the test was taken as relative film resistance.

2.3. Photocatalytic experiments

The photocatalytic activity was assessed using the methylene blue (MB) degradation test. MB, an organic dye with molecular formula $C_{16}H_{18}ClN_3S$, is often used as a model pollutant to assess the activity of the photocatalyst [17]. For the photodegradation kinetics investigation, 500 mL of 10 mg L^{-1} MB solution was poured in a borosilicate cylindrical glass vessel with 100 mm diameter and 120 mm height. A quartz glass tube was placed in the vessel, near the side wall. A glass having 50 × 70 mm thin film area was placed opposite the tube, with the coated side facing the tube. The distance between the tube and the glass was 50 mm. Pen Ray lamp (UVP Products Cat. No. 90–0012–01), with radiation wavelength of 254 nm and emission intensity of 2 mW cm^{-2}, was placed inside the quartz tube. The solution was first stirred for 30 min to establish the adsorption equilibrium and no change in concentration has been noted through that period. After 30 min the lamp was switched on and the photodegradation experiment was carried out at 25 °C.

In order to determine methylene blue concentration, the aliquots of 4 mL were withdrawn from the suspension at appropriate time intervals. The concentrations were determined using UV–visible spectrophotometer Varian, Cary 1E. For monitoring the concentration of MB, and hence its degradation, absorption peak height at wavelength of 664 nm (where it was maximal) was used. Methylene blue concentration has been computed using a previously established calibration curve.

The photodegradation kinetics of MB was analysed using the Langmuir–Hinshelwood model [18]. When the pollutant amount is in the millimolar concentration range, the reaction rate R is proportional to the surface coverage θ according to equation [18]: