



Size-controlled synthesis of anatase nanobrush structures with higher crystal density



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ABSTRACT

Titanium dioxide was synthesized in multistep process applying of AAO (Anode Aluminum Oxide) as a template. The TiO₂ nanowires were obtained by deposition of titanium precursors inside the pores of AAO membranes (non-hydrolytic sol-gel technique), calcined at 875 K with subsequent removal of alumina matrix by leaching it with phosphoric acid. During the AAO synthesis, it was proved that the electrical work can serve as the unified factor influencing the amount of formed AAO. The diameters of obtained titania nanowires were consequence of used AAO membranes. The higher density of titania elementary cell was observed for all synthesized nanostructures. It was confirmed by XRD and SAED measurements. The TiO₂ nanowires attached vertically to polymer disc (50 mm diameter) were used in photocatalytic decomposition of methyl orange. All nanomaterials showed ten times higher photocatalytic activity than P-25. High photoactivity of obtained material is related to external area of vertically aligned titania nanowires.

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1. Introduction

Titanium dioxide is well known material used nowadays in numerous applications. Since early seventies of 20th century the semiconducting properties of this material due to light absorption ability attracted attention of many research groups working in photocatalysis, photoelectrochemistry or electrochemistry [1–4]. However, relatively large value of band gap (BG) of ~3.2 eV do not allow to apply for these purposes the visible part of light spectrum. Moreover, the amount of light excited electrons can be reduced significantly during recombination process between excited electrons and positively charges holes. The crystallographic defects both in anatase and rutile phases as well as presence of foreign ions in titania structure are responsible for lowering the quantum yield [5,6].

The development of nanoscale materials opened new possibilities in photocatalysis and other light induced processes [7,8]. The amount of recombination sites of excited electrons and positively charged holes due to the “nanoscale effect” can be significantly reduced in these materials. Much lower diffusion of excited charge within the bulk of solid with small dimensions resulted in much

higher density of charges on the surface what in consequence leads to much higher activity.

Recent studies indicate that four basic methods and their derivatives concerning nanostructural synthesis of TiO₂ can be involved. The most popular techniques are, solvothermal, sol-gel, direct electrochemical oxidation of titanium and hard template method [9–15]. Application of those methods can result in larger variety of structures, from spherical to cylindrical forms. Considering high level of control during synthesis, two of them should be highlighted, anodic oxidation of titanium foil and hard templating method with anodic aluminum oxide (AAO). These techniques not only allow for dimensions and shape control but also their spatial orientation. Additionally, the AAO templates can be used to obtain other nanomaterial than titania, eg. other nanostructured oxides or metals [15–19]. Therefore, at this technique focuses herein.

This paper proposes synthesis of titania matrices with the shape of vertical nanowires attached to polymer film as efficient catalysts for photocatalytical applications. In contrast to majority of works in which AAO was prepared from very pure alumina (99.999%) in this paper synthesis was based on aluminum foil with purity of 99.5%. Moreover, it was decided to use the non-hydrolytic sol-gel technique (NHSG) [20,21] as a method for the incorporation of the titanium oxide (IV) to the porous structure of the AAO what according to our knowledge, it has been carried out for the first time. The reason for this change is based on easier penetration of

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the AAO pores during synthesis of TiO₂. The use of standard sol-gel methods for incorporation of the oxide layer has some limitation and mainly is used with AAO pores opened from both sides [17,18,22].

Total photooxidation of organic pollutants in aqueous phase is based on photogeneration of HO[•] radicals originating from water via formation of OH- groups on titania surface. These radicals can be effectively used in photocatalytic detoxification of water and pollutant removal of aqueous effluents. Among numerous organic contaminations of water such dyes as methylene blue, rhodamine B or methyl orange are representative organic compounds which can be mineralized by this method. In present paper decomposition of methyl orange was applied as a test reaction in photocatalytic activity of synthesized titania nanowires.

2. Materials and methods

2.1. Preparation of AAO matrices

Aluminum foil with thickness of 0.1 mm and purity of 99.5% was applied (Table 1). Anodic aluminum oxidation process was performed in the poly(methyl methacrylate) cell of our own design in which aluminum discs of 55 mm diameter (23.75 cm²) were mounted as anode. The applied area of anodization was 18.10 cm². Cathode was made of graphite. Distance between electrodes was 4 cm. Oxalic acid (0.3 M) and phosphoric acid (0.42 M) were applied as electrolytes. The applied voltage was 50 or 60 V (oxalic acid) and in experiments with phosphoric acid it varied between 100 and 200 V (20 V intervals). A constant temperature (288 K) of anodization process was controlled by external cooling with flowing electrolyte. Two programmable power units (DS 14100 from Motech) controlled by external computer were used in anodization process. The adjustment of current density at the level of 5.3 mA cm⁻² was realized with a series of resistors connected into the circuit.

In experiments with phosphoric acid as electrolyte the two step anodization process was applied. In the first one, anodization process at indicated voltage lasted 60 min. After removal of anode from the cell, it was treated for 90 min at room temperature with solution containing 1.2 M H₃PO₄ and 0.3 M of chromium oxide, next washed several times with distilled water and finally anodized (second step) in an electrochemical cell at the same voltage as in the first one until the system reached the value of 19 kJ. After removal from the cell and final treatment with 10 vol.% H₃PO₄ (15 min) samples were next washed with distilled water and dried in air at room temperature for 24 h.

2.2. Preparation of titanium oxide nanowires

Samples with different texture of AAO attached to non reacted aluminum discs were placed in reaction vessel equipped with reflux, rubber septum and three-way vacuum valve. Samples after purging with argon (15 min), activation at 625 K under vacuum

(3 hs at 10⁻⁵ Pa) and subsequent cooling to room temperature were covered carefully by 250 cm³ dried toluene solution containing 0.004 M of Ti(isoPrO)₄ and 0.0018 M of TiCl₄. Next, samples were kept at boiling point of toluene for 3 h under reflux. After cooling additional amounts of Ti(isoPrO)₄ (8.2·10⁻⁵ M) and TiCl₄ (22.1·10⁻⁵ M) were injected into the reaction vessel. Samples were kept again at b.p. of toluene under reflux for another 3 h. After cooling, the Al/Al₂O₃/TiO₂ discs were carefully washed with isopropyl alcohol and distilled water. After 12 h of drying at 388 K samples were calcined for 6 h at 875 K (heating rate 1 K/min) followed by ultrasonic bath (10 min).

The aluminum discs containing AAO and deposited titania were covered only from one side (TiO₂) with two layers of polymer film (Epidian[®] 6, 0.5 mm thick). First layer was a pure resin, whereas the second contained glass fiber suspended. After 20 h of polymer hardening, the non reacted aluminum foil with AAO layer was dissolved (20 h) at room temperature in 1 M solution of KOH. The alumina traces were removed with H₃PO₄ (10 vol.%) for 20 h. The titania nanowires/polymer systems finally were washed with distilled water and dried in air at R.T.

2.3. Photocatalytic activity tests

Titania nanowire discs (44.5 mm diameter) were centrally placed in flat plate photoreactor [23] filled with 220 cm³ water solution of methyl orange (50 μM). Photocatalytic activity tests during methyl orange decomposition were performed in air flowing through photoreactor with the rate of 3 dm³/h under light intensity of 186 W m⁻² (19 klx). The 300 W Ultra Vitalux bulb from Osram was applied as light source operating mainly within visible region of light spectrum (only 5.5% represented UV). Reactor window was from Pyrex glass. Each experiment started with 3 h exposure of titania nanowires to methyl orange solution without illumination. Next the photocatalytic reaction started and lasted 48 h. Photocatalytic activity was controlled in 6 h intervals measuring changes in dye absorption value at 465 nm with UV-vis spectrometer (Cary 100 Bio from Varian). In order to assure appropriate certainty and accuracy of measurements all photocatalytic tests were performed in five-fold repetitions.

P-25 titania attached to polymer film disc with identical dimensions of as nanowire disc was applied as the reference.

The reference sample was made by dispersion onto the wet resin disc with the P-25 powder, so that an entire surface was covered. The unbound P-25 was removed by stream of compressed air after complete crosslinking of the resin.

In additional experiment the filter from ordinary soda glass was located between photoreactor and Vitalux bulb. The filter was used to cut off the influence of UV radiation on photocatalytic activity. The distance between photoreactor, soda glass plate and bulb was 20 and 50 cm, respectively.

2.4. Characterization

Chemical composition of applied aluminum as well as AAO was performed with the emission spectrometer ICP-OES VISTA-MPX spectrometer. Both AAO and TiO₂ nanowires were characterized by X-ray diffraction (XRD) measurement (Bruker AXS D8 Advance calibrated with Si external standard). Morphology and texture of AAO and TiO₂ nanowires was measured by SEM (Evo 40, Zeiss, 17 kV for samples prepared with oxalic acid and Jeol 7001TTLS for samples synthesized in presence of phosphoric acid) spectroscopy. The HRTEM with SAED (Jeol ARM200F, 200 kV) was used to confirm the presence crystal structure. The UV-vis transmittance and diffuse reflectance spectroscopy were performed with Cary 100 Bio from Varian spectrometer equipped with integrating sphere (for solids).

Table 1

Composition of applied aluminum foil and AAO's membranes measured with ICP-OES.

Sample origin	Elements content [ppm]							
	Cr	Fe	Mg	Mn	Ni	Ti	V	Zn
Al foil	13.6 ^a	2500 ^a	20.3 ^a	36.6 ^a	12 ^a	173 ^a	11.3 ^a	263 ^a
AAO ^b	13.0	93.0	5.9	21.0	16.0	174.0	12.0	258.0
AAO ^c	7.9	20.0	2.8	11.0	1.4	95.0	6.7	187.0

^a Expressed as content in Al₂O₃.

^b Prepared in presence of H₂C₂O₄.

^c Prepared in presence of H₃PO₄.

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