



Effects of heat and peroxide treatment on photocatalytic activity of titanate nanotubes



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ABSTRACT

The influence of structural, morphological and surface properties on photocatalytic activity of pristine and modified titanate nanotubes was carefully described and discussed in the following study. Titanate nanotubes (TNTs) were prepared via alkaline hydrothermal synthesis route followed by acid washing at ambient conditions. The resulting high specific surface area nanotubular solids were further modified by two distinguished post-treatments: (i) heat-treatment in the temperature range from 300 to 700 °C, and (ii) peroxide-treatment at room temperature. Bisphenol A (BPA), a well-known endocrine disrupting compound (EDC), was selected as a testing molecule to evaluate the photodegradation potency of the modified TNTs. The resulting BPA and TOC removals confirmed that crystallinity and BET surface area of examined heat-treated solids play a crucial role in governing the photooxidation reaction. Regarding the peroxide-treated TNTs, a nearly three-fold improvement in BPA removal was attained in comparison to the pristine TNTs, which can be attributed to the redox reaction of surface titanium(IV) peroxo groups. However, the exposure of anatase-based samples to the H₂O₂ medium resulted in deteriorated photocatalytic oxidation of the model compound, due to recovery of surface Ti³⁺ defect sites, leading to increased e⁻-h⁺ recombination and decreased oxygen adsorption. In addition, a carbon-based elemental analysis of the heat-treated TNTs (TNT_500) and standard TiO₂ P25 stressed the potential of tailor-made crystalline TNTs to be applied as photocatalysts for long-term removal of aqueous organics, due to low accumulation of carbonaceous deposits during the photodegradation runs.

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1. Introduction

The expansion of photocatalytic applications based on TiO₂ was triggered by the pioneering work of Fujishima and Honda in 1972 on electrochemical photolysis of water over single crystal TiO₂ [1]. Fine semiconductor materials are ideal due to their chemical stability, nontoxicity and high photocatalytic reactivity. They are widely used in the elimination of pollutants, gas sensing and fabrication of solar cells [2]. The physicochemical properties of nanoparticles can be tailored by their structural and surface properties, such as size, morphology, crystallinity and surface functional groups. For instance, the recently discovered synergistic effect that takes place in mixed-phase (e.g., anatase-rutile) nanocomposites can additionally improve charge separation, thereby increasing their photocatalytic activity [3]. On account of this phenomenon, which stimulates a spatial separation of carriers and thus reduces their

recombination, the commercial TiO₂ P25 Degussa has become the most widely used photocatalyst.

Recently, elongated nanostructured titanates such as nanotubes (NTs), nanoribbons and nanofibers have attracted a lot of attention due to their unique physicochemical properties and improved performance in various applications [4]. Titanate nanotubes (TNTs) are among high aspect ratio titanate nanostructures famous for their high specific surface area, which facilitates various catalytic reactions. Namely, such structures are often used as supports in heterogeneous catalytic processes, since high catalyst dispersion can be achieved, while the open mesopores permit efficient transport of reactants and products [5]. The photocatalytic activity of the as-prepared TNTs was found to be markedly lower than that of the standard TiO₂ P25 in the reaction of NH₃ oxidation [6], as well as in the reaction of dye oxidation in aqueous suspensions [7]. This can be either attributed to Na⁺ impurities acting as recombination centres or low crystallinity of the as-prepared nanotubular particles.

TNTs are in general synthesized by three different approaches: (i) the chemical (template assisted) method [8], (ii) electrochemical anodic oxidation [9], and (iii) alkaline hydrothermal method [10].

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Among these methods, hydrothermal treatment has attracted the most attention due to its cost-effectiveness and simplicity. Owing to the low photocatalytic activity of the pristine TNTs, further improvements in activity are necessary to meet and, ultimately, to exceed the photocatalytic properties of the standard material TiO₂ P25. A widespread and efficient method for improvement in activity of TNTs is focused on structure transformation to the more photocatalytically active phases of TiO₂. The layered structure of protonated polytitanates can be efficiently transformed to crystalline TiO₂ polymorphs by heat-treatment at elevated temperatures (usually above 400 °C). In this way, the as-modified (at different temperatures) solids with diverse crystal-phase compositions, morphologies, pore structures and surface properties exhibit a great interest to be examined in various photocatalytic processes. An increased photocatalytic activity is accompanied by an improvement of nanostructure crystallinity; however, a further increase in calcination temperature (above 500 °C) results in lower photocatalytic activity, due to stripping off the surface OH⁻ groups and a reduction in the surface area of nanostructures [11].

An alternative to heat treatment is the acid hydrothermal treatment of protonated TNTs with residues of HCl at 200 °C [12], or with HNO₃ at 180 °C [13], which results in the formation of nanostructured anatase with a fibrous or particulate morphology. In this way, the synthesis temperature is significantly reduced and the surface OH⁻ groups are kept intact, resulting in highly photocatalytically active solids for oxidation of model organic dyes [14]. Other attempts to outperform the commercial TiO₂ P25 have generated a large array of photocatalyst synthesis techniques. For example, depositing fine noble metals (e.g., Pt, Ag, Au, Pd and Rh) on the photocatalyst surface is a standard practice for enhancing charge separation. This establishes a Schottky barrier via Fermi level equilibration between the photocatalyst and metal deposits [15]. Photocatalyst doping, either with metal or non-metal ion, is also commonly employed to extend the photoresponse of a material toward lower energy excitation and/or to enhance the net separation of photogenerated charges [16]. Recently, the tendency towards high photocatalytic activity of TNTs dictates the surface modifications, such as fluorination and phosphation, which are expected to retard the phase transition from titanate nanotubes to titania nanoparticles. Accordingly, it is possible to obtain high specific surface area titania-titanate nanotube structures with efficient photocatalytic activities [17].

In the present study, protonated titanate nanotubes with specific surface area approaching 400 m² g⁻¹ were synthesized under alkaline hydrothermal reaction conditions followed by thorough acid rinsing. The physicochemical properties of the as-prepared TNTs were then modified by two distinguished methods: (i) heat-treatment in the temperature range from 300 to 700 °C, and (ii) chemical treatment with the concentrated H₂O₂ solution. The calcination accompanied by the phase transformation resulted in the formation of photocatalysts with diverse textural, morphological and surface properties. On the other hand, a dense coverage with OH⁻ groups of the as-prepared TNTs enabled the formation of titanium(IV) peroxo groups (reaction with the H₂O₂ solution), which could be utilized in surface redox reactions. The influence of phase composition, particle size, morphology and surface chemistry on photocatalytic activity was examined in photocatalytic oxidation reaction of a model pollutant bisphenol A (BPA) dissolved in water. The photolytic/photocatalytic BPA degradation experiments were conducted in a Pyrex glass reactor under irradiation of UV high-pressure mercury lamp. The textural, surface and morphological properties of tested photocatalysts were investigated using SEM, XRD, UV-Vis-DR, FTIR-ATR, TGA and BET analytical techniques. The CHNS elemental analysis of fresh and spent catalysts was applied to evaluate the amount of carbonaceous deposits accumulated during the photocatalytic experiments, with a view to estimate the

suitability of TNT-based photocatalysts for a long-term removal of emerging organic compounds.

2. Experimental

2.1. Catalyst preparation

The catalysts examined in this study were based on high specific surface area titanate nanotubes (TNTs), which were prepared using alkaline hydrothermal synthesis similar to that reported by Kasuga et al. [10]. In a typical synthesis procedure, 2 g of commercial TiO₂ powder (P25, Degussa) was dispersed in a concentrated caustic solution (10 M NaOH) by means of ultrasonic homogenizer. The alkali dispersion was then poured in a 200 mL Teflon-lined autoclave and held at 130 °C for 24 h. The resulting white precipitates were separated from reaction solution by filtration process, followed by thorough rinsing with deionized water, in order to neutralize the product. These sodium titanates were further treated with diluted HCl solution (0.1 M) with the intention of topotactic cation exchange. After the protonation process, TNTs were neutralized with deionized water for a second time and finally dried in vacuum under cryogenic conditions. With regard to the main purpose of this study, i.e., to examine the influence of different structural, morphological and surface properties of various TNT-based photocatalysts on the removal of a model organic pollutant, the as-synthesized nanotubular solids were further modified by two distinguished routes: (i) heat-treatment in the temperature range from 300 to 700 °C in steps of 100 °C, and (ii) chemical functionalization using the concentrated solution of H₂O₂. The heat-treatment was performed in a tubular furnace in air atmosphere, where the samples were kept at annealing plateau for 1 h. The calcined samples were denoted as TNT_300, TNT_400, etc. On the contrary, the H₂O₂ functionalization (i.e., formation of surface titanium(IV) peroxo groups) was conducted under ambient conditions varying only the time of exposure to oxidizing solution (30% H₂O₂, Aldrich). The TNT powders were suspended in concentrated peroxide solution and magnetically stirred for 1 min, 1 h and 10 h, respectively. These samples were designated as TNT.H₂O₂.1 min, TNT.H₂O₂.1 h, etc. After H₂O₂ functionalization, titanate nanotubes were rinsed with deionized water to remove surplus H₂O₂ and dried at 40 °C. In addition, to examine the influence of peroxide treatment on the crystalline samples, the commercial TiO₂ P25 and heat-treated TNTs at 500 °C (TNT_500) were included in a comparative study as well. These two samples were exposed to the H₂O₂ solution for 1 h and, accordingly, designated as P25.H₂O₂.1 h and TNT_500.H₂O₂.1 h, respectively.

2.2. Catalyst characterization

The as-prepared as well as the modified photocatalyst samples were thoroughly characterized, using a variety of characterization techniques, in order to examine surface, textural and morphological particle properties. The morphology and particle size of synthesized solids was examined by field-emission scanning electron microscope (FE-SEM SUPRA 35VP, Carl Zeiss), equipped with energy-dispersive detector (Inca 400, Oxford Instruments). The phase composition was determined from the collected X-ray powder diffraction patterns of the catalysts. PANalytical X'pert PRO MPD diffractometer using Cu K α 1 radiation (1.54056 Å) in reflection geometry was applied for the measurement of Bragg diffractions. The data were collected in the range between 10 and 90° in steps of 0.034°. Crystalline phases were identified by comparison with PDF standards from the International Centre for Diffraction Data (ICDD). Specific surface area, total pore volume and average pore width of the catalysts were determined from

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